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Calculation of Vibrational and Electronic Excited-State Absorption Spectra of Arsenic-Water Complexes Using Density Functional Theory

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14. ABSTRACT
Calculations are presented of vibrational and electronic excited-state absorption spectra for As-H_2O complexes using density functional theory (DFT) and time-dependent density functional theory (TD-DFT). DFT and TD-DFT can provide interpretation of absorption spectra with respect to molecular structure for excitation by electromagnetic waves at frequencies within the IR and UV-visible ranges. The absorption spectrum corresponding to excitation states of As-H_2O complexes consisting of relatively small numbers of water molecules should be associated with response features that are intermediate between that of isolated molecules and that of a bulk system. DFT and TD-DFT calculated absorption spectra represent quantitative estimates that can be correlated with additional information obtained from laboratory measurements and other types of theory based calculations. The DFT software GAUSSIAN was used for the calculations of excitation states presented here.

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Contents

Introduction

The present study examines properties of Arsenic-water (As-H_2O) complexes and is based on significant progress in density functional theory (DFT), time-dependent density functional theory (TD-DFT), and associated software technology, which is sufficiently mature for the determination of dielectric response structure, and should actually provide complementary information to that obtained from experiment [1-7]. This complementary information should be in terms of the physical interpretation of spectral features with respect to molecular structure.

Previous studies have examined various properties of water molecules and their clusters [8-16]. As emphasized previously [17], the absorption spectrum of H_2O clusters should be of significance for interpretation of absorption spectra associated with spectroscopic detection of chemicals, which are within an ambient water environment. Our studies of water clusters [17] showed that the calculations of ground state resonance structures, and absorption spectra at THz vibrational frequencies of IR spectra are correlated with experimental measurements. This paper presents calculations of vibrational and electronic excited state resonance structures associated with arsenic-water complexes consisting of relatively small numbers of water molecules using DFT and TD-DFT. Calculation of excited state resonance structure using DFT and TD-DFT can provide interpretation of absorption spectra with respect to molecular structure for excitation by electromagnetic waves at frequencies within IR and UV-visible ranges. The absorption spectrum of an As-H_2O complex consisting of a given number of water molecules should be associated with response features that are intermediate between that of isolated molecules and that of a bulk lattice. In principle, these absorption spectra should provide quantitative estimates of spectral response features that can be correlated with additional information obtained from laboratory measurements and other types of theory based calculations, or conversely, adapted as constraints for the inverse analysis of experimentally measured absorption spectra. A significant aspect of using DFT and TD-DFT for the calculation of absorption spectra is that it adopts the perspective of computational physics, according to which a numerical simulation represents another source of "experimental" data. The absorption spectrum of As-H_2O complexes should be of significance for interpretation of absorption spectra associated with detection in practice. This follows in that most environments associated with detection in practice include the presence of water in one form or another. These forms can range from isolated molecules in gas phase, molecular clusters, adsorbed surface layers, droplets and interface regions in liquid phase, and ice. Absorption spectra of molecular clusters consisting of water represent a separate regime for dielectric response with respect to electromagnetic wave excitation. This regime should be better quantified for improved interpretation of absorption spectra associated with systems that include water complexes as components.

A review the formal mathematical structure underlying DFT calculations, as well as the procedure for calculation of absorption spectra corresponding to vibrational states, has been given elsewhere [17]. The extension of DFT for the calculation of absorption spectra corresponding to electronic excitation states, which is the formalism of time-dependent density functional theory (TD-DFT), is described in reference [18].

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The present study examines properties of As-H_2O complexes using quantum-theory based calculations. These properties are the vibrational and electronic excited state absorption spectra of As-H_2O complexes, which are calculated using DFT and TD-DFT. This study presents analysis of calculated spectra for As-H_2O complexes based on comparison with calculated spectra for molecular clusters of H_2O, and a compilation of vibrational and electronic excited state absorption spectra for As-H_2O complexes, which are for further analysis. The software GAUSSIAN09 (G09) [7] was used for the calculation of excited state structures.

Analysis of Spectra

Presented in this section is a preliminary analysis of vibrational and electronic excited state absorption spectra for As-H_2O complexes calculated using DFT and TD-DFT, which is based on comparison with calculated spectra for molecular clusters of H_2O.

Vibrational resonance structure of As-H_2O complexes

Results of a computational investigation using DFT concerning As-H_2O complexes are presented. These results include the relaxed or equilibrium configuration of the As-H_2O complexes' ground-state oscillation frequencies and IR intensities for As-H_2O complex geometries having stable structures, which are calculated by DFT. For these calculations geometry optimization and vibrational analysis was effected using the DFT model B3LYP [29, 30] and basis function 6-311+G(d) [31, 32]. These basis functions designate the 6-311G basis set supplemented by diffuse function: +, and polarization function: (d), having one set of d functions on heavy atoms [33]. A graphical representation of molecular geometries of As-H_2O complexes consisting of 1 molecule of arsenic and 2, 5, and 24 water molecules are shown in Fig. (1). For comparison, relaxed water clusters without As are shown in Fig. (2). In response to the presence of As molecule, the positions of water molecules are rearranged at distances beyond of the nearest neighbors (See Fig. (2)). IR intensities as a function of frequency for As-H_2O complexes consisting of 2, 5 and 24 water molecules are shown in Fig. (3). For comparison, Fig. 4 shows vibrational resonances for corresponding water clusters without As. With increased size of a cluster, the resonance structure broadens around single water molecule resonances, approximately 1700, 3425 and 3575 cm^{-1}, as well as development of a low frequency band below the lowest resonance, approximately 1700 cm^{-1}. Comparison of the vibrational spectra in Fig. 3 and Fig. 4, shows that resonance structure is modified by the presence of As for a wide range of frequencies.

Electronic excited state resonance structure of As-H_2O complexes

Results of a computational investigation using TD-DFT concerning As-H_2O complexes are presented. These results include the oscillator strength as a function of excitation energy (within the UV range) for different geometries of the interacting systems associated with stable structures, which are calculated by DFT as described above. The oscillator strength (UV intensity) as a function of excitation energy for the As-H_2O complexes consisting of 2, 5 and 24 water molecules are shown in Figs. (5). The effect of the As molecule on the UV spectra can be seen by comparison with the electronic excitation spectrum of corresponding water clusters without As (see Fig. (6)). In the presence of As, a new line appears near 220 nm, below the absorption edge of water clusters (see Fig. (6)),

which is around 200 nm, and is red-shifted relative to the absorption of a single water molecule at 164 nm. This red-shifting is expected for the DFT calculations, which is not consistent with observed blue-shifting for liquid and ice phases compared to vapor [23,24]. Accordingly, DFT calculated band edge frequencies in clusters should be corrected by accounting for reduction in the binding energy of an electron-hole pair extending over near neighbor molecules [24].

A Compilation of Spectra for As-H_2O complexes

Presented in this section is a compilation of vibrational and electronic excited state absorption spectra for As-H_2O complexes calculated using DFT and TD-DFT. Shown in Fig. (7) are molecular geometries of As-H_2O complexes after geometry optimization, without the presence of a water solvent background. Given in Table 1 are DFT calculated IR spectra for the optimized geometries of As-H_2O complexes shown in Fig. (7). Shown in Figs. (8) and (9) are IR and UV spectra, respectively, for the optimized geometries of As-H_2O complexes shown in Fig. (7). Shown in Fig. (10) are molecular geometries of As-H_2O complexes after geometry optimization, with the presence of a water solvent background. Given in Table 2 are DFT calculated IR spectra for the optimized geometries of As-H_2O complexes shown in Fig. (10). Shown in Figs. (11) and (12) are IR and UV spectra, respectively, for the optimized geometries of As-H_2O complexes shown in Fig. (10). Given in Tables 3 and 4 are energies for optimized geometries and excited states, respectively, of the As^{+3} - nH_2O clusters shown in Figs. (7) and (10).

Conclusion

The DFT and TD-DFT calculated absorption spectra given here provide information concerning molecular level dielectric response structure. The calculations of vibrational and excited state resonance structure associated with As-H_2O complexes using DFT and TD-DFT, respectively, are meant to serve as reasonable estimates of molecular level response characteristics, providing interpretation of dielectric response features with respect to molecular structure, for subsequent adjustment relative to experimental measurements and additional constraints based on molecular structure theory. We have in this paper studied As-H_2O complexes in order to quantify interpretation of their absorption spectra.

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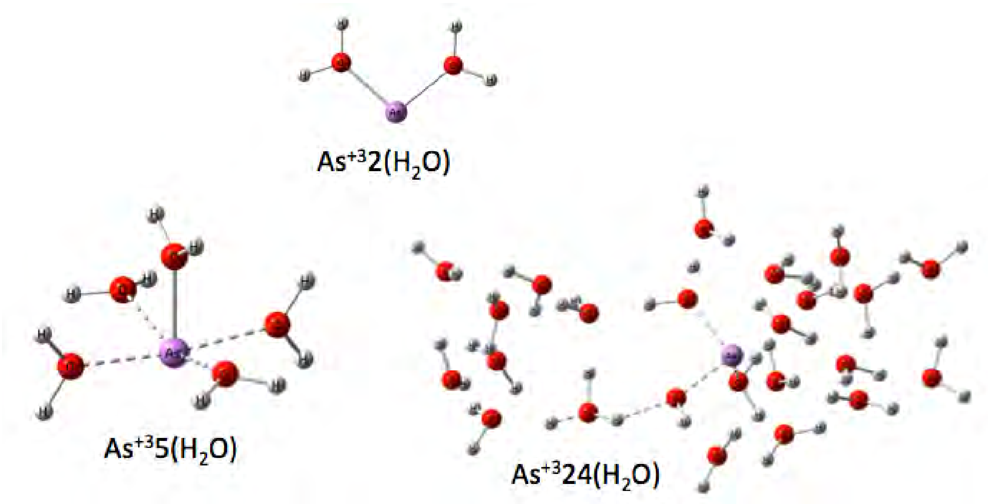

Figure 1. Molecular geometries of As-H_2O complexes consisting of 2, 5 and 24 water molecules.

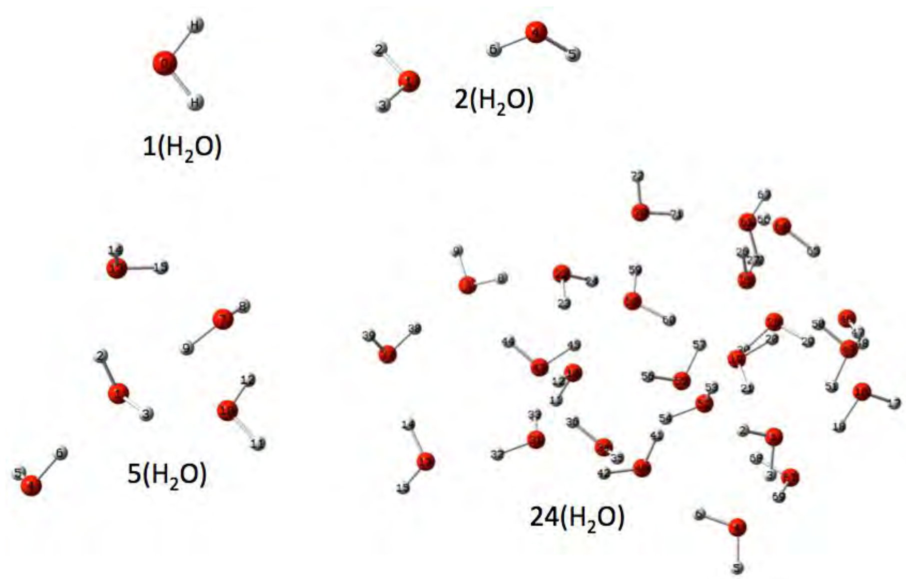

Figure 2. Molecular geometries of water molecule and water clusters 2, 5 and 24 molecules.

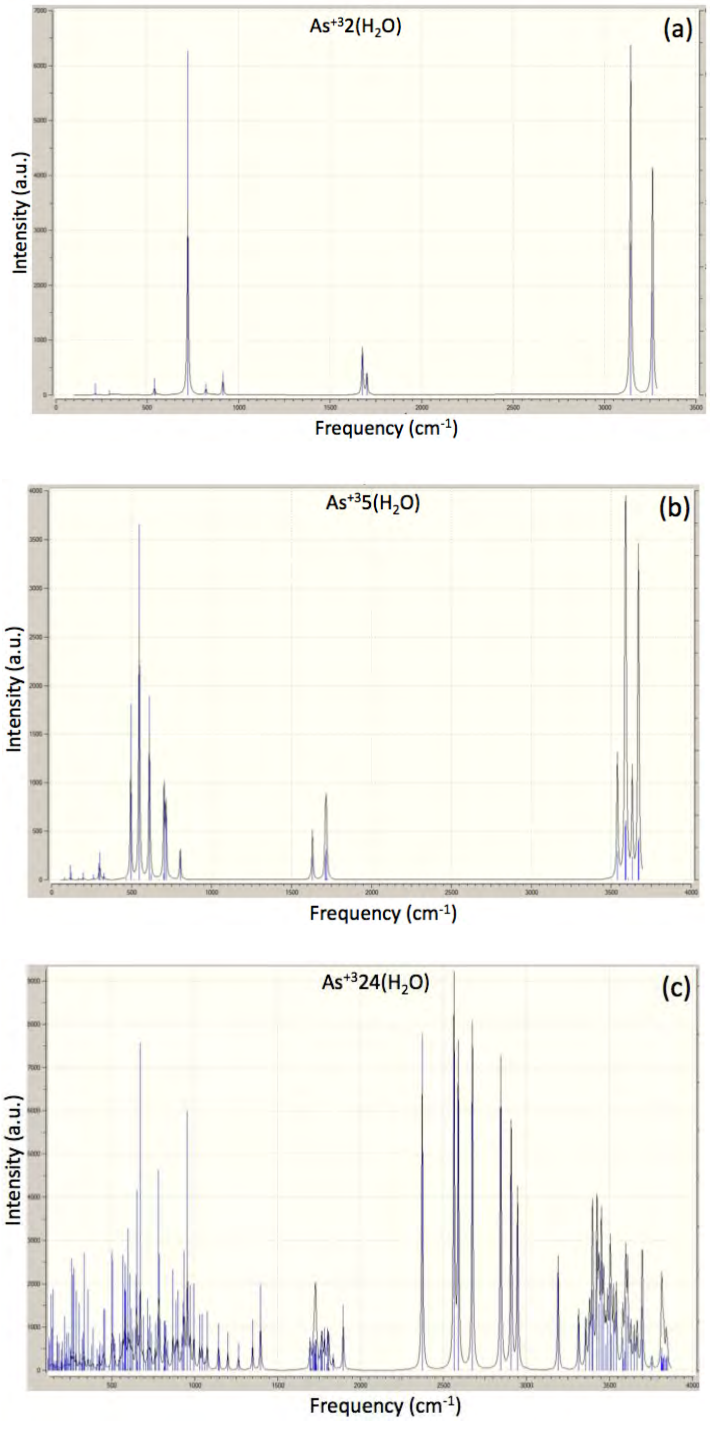

Figure 3. DFT calculated IR spectra for As-H_2O complexes consisting of (a) 2, (b) 5 and (d) 24 water molecules.

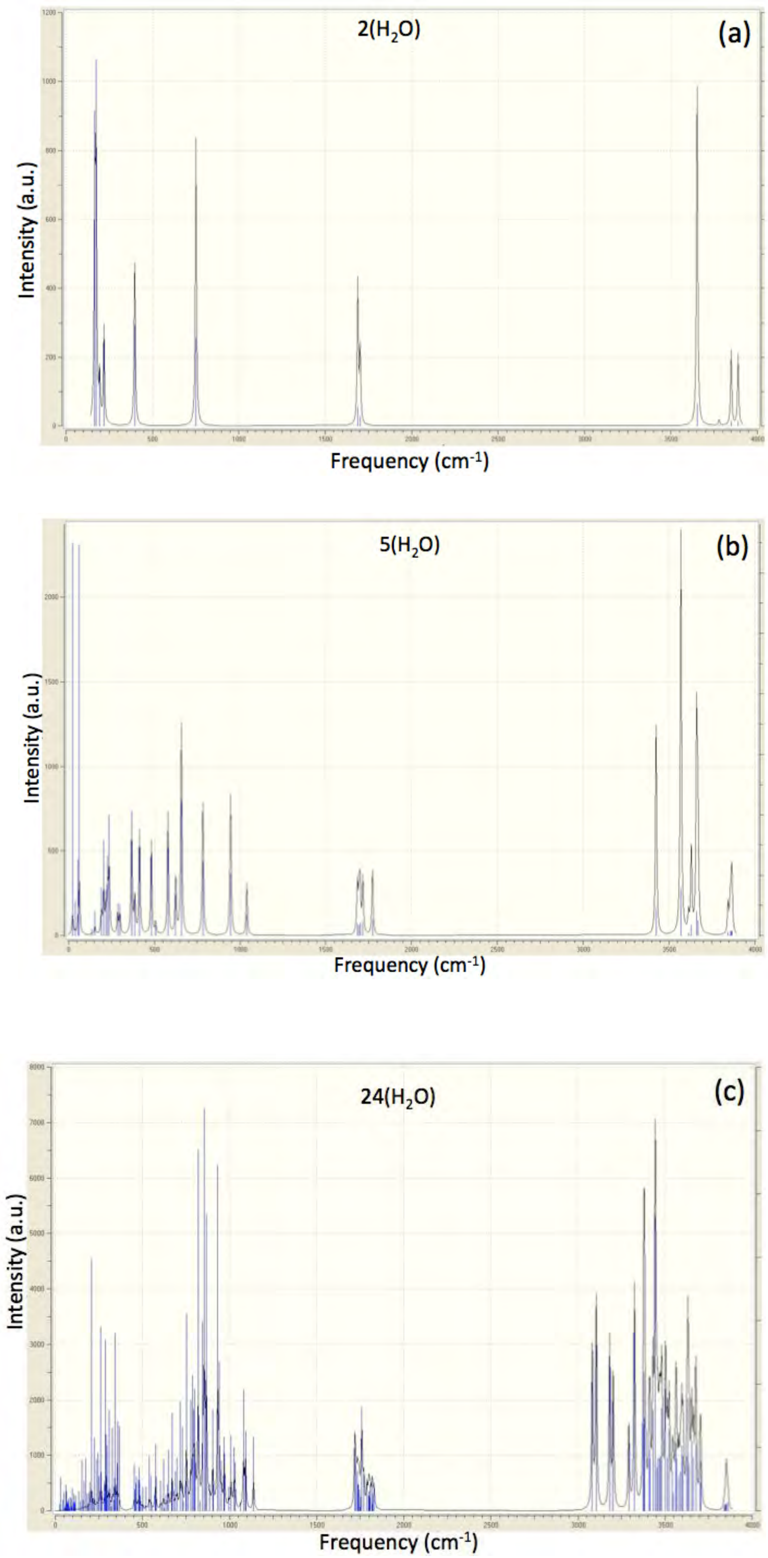

Figure 4. DFT calculated IR spectra for water clusters consisting of (a) 2, (b) 5 and (c) 24 molecules.

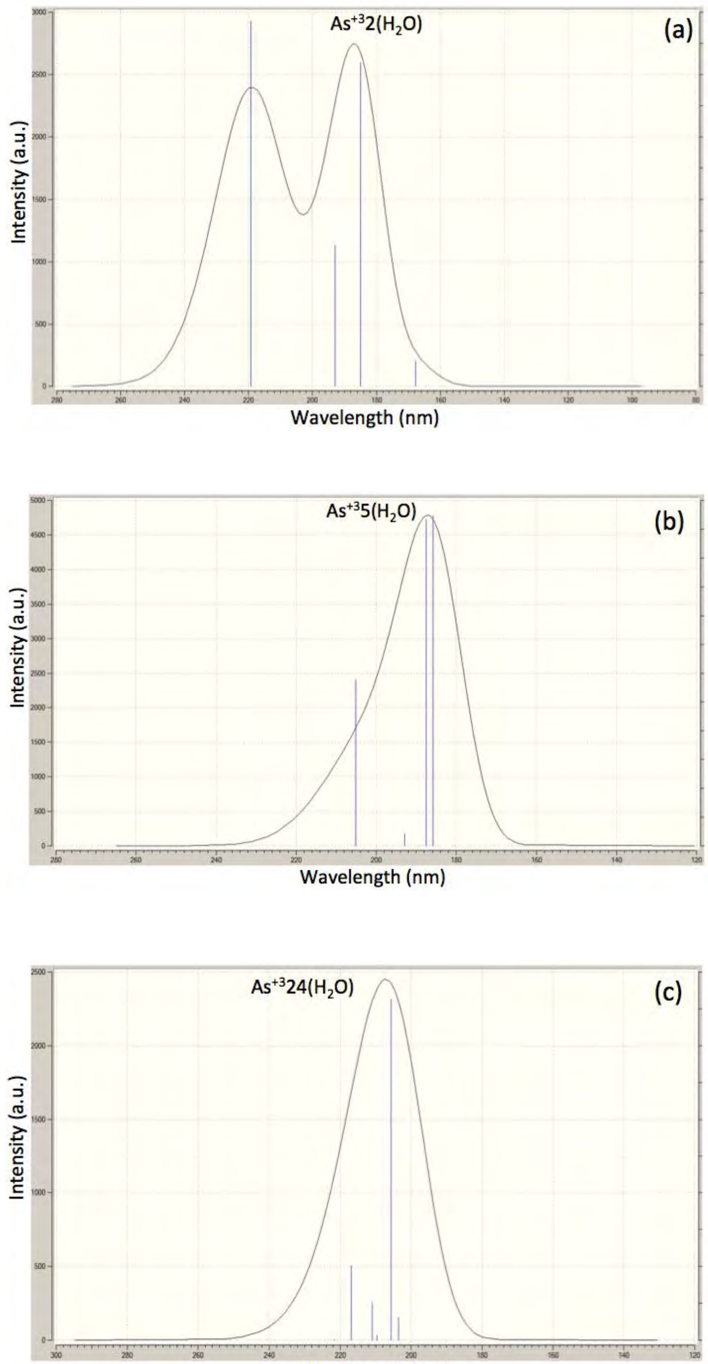

Figure 5. TD-DFT calculated UV-Visible spectra for As-H_2O complexes consisting of (a) 2, (b) 5 and (d) 24 water molecules.

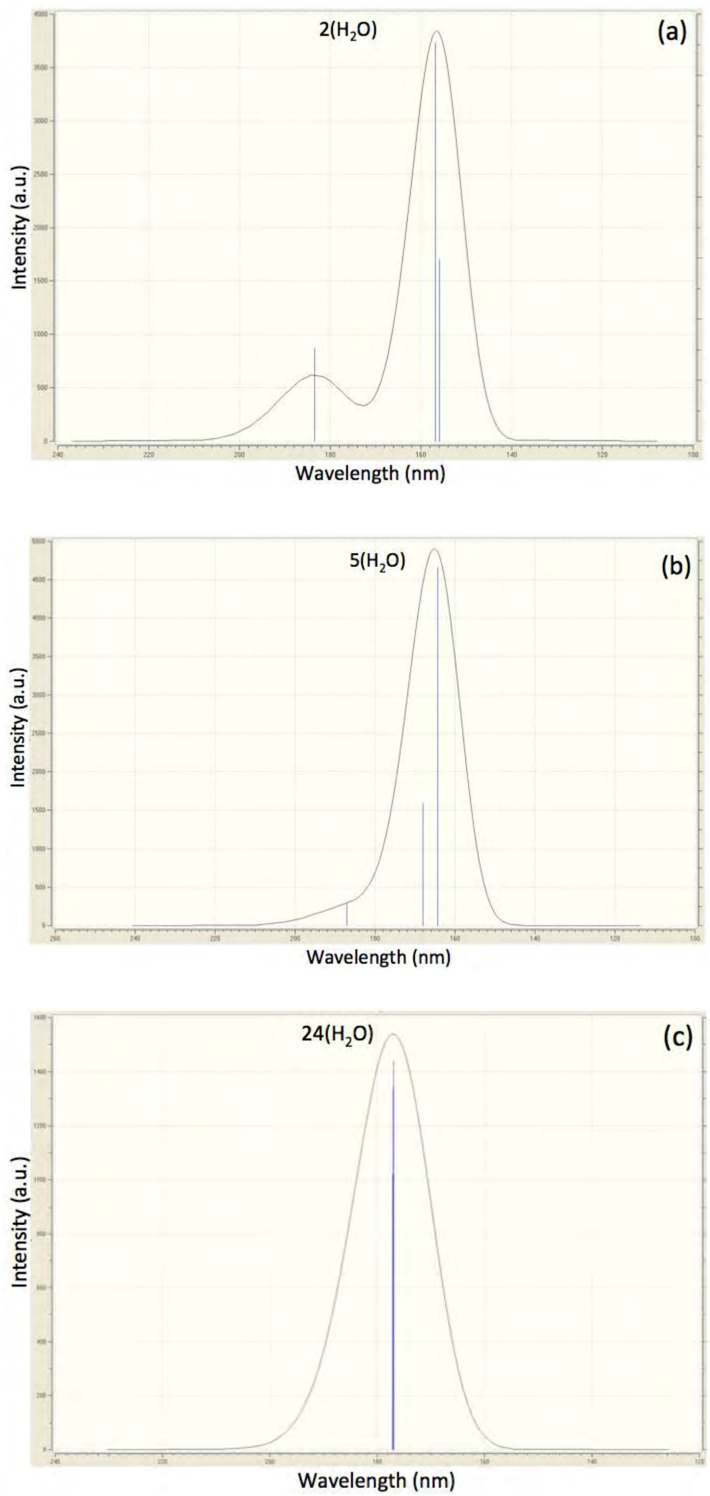

Figure 6. TD-DFT calculated IR spectra for water clusters consisting of (a) 2, (b) 5 and (c) 24 molecules.

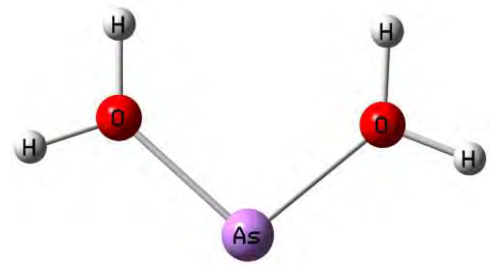

Figure 7a. As^{+3} $2(H_2O)$

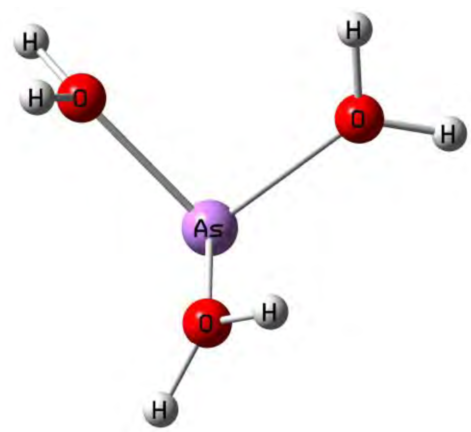

Figure 7b. As^{+3} $3(H_2O)$

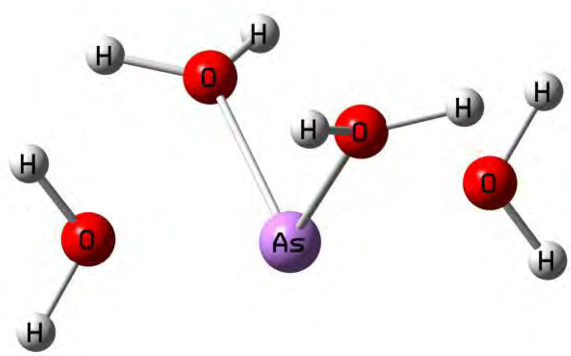

Figure 7c. As^{+3} $4(H_2O)$

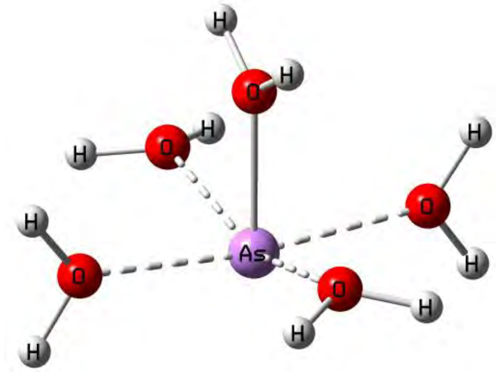

Figure 7d. As^{+3} $5(H_2O)$

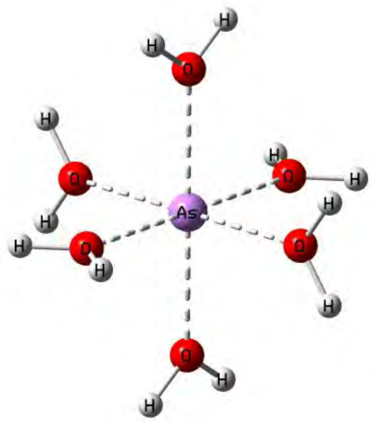
Figure 7e. As^{+3} $6(H_2O)$

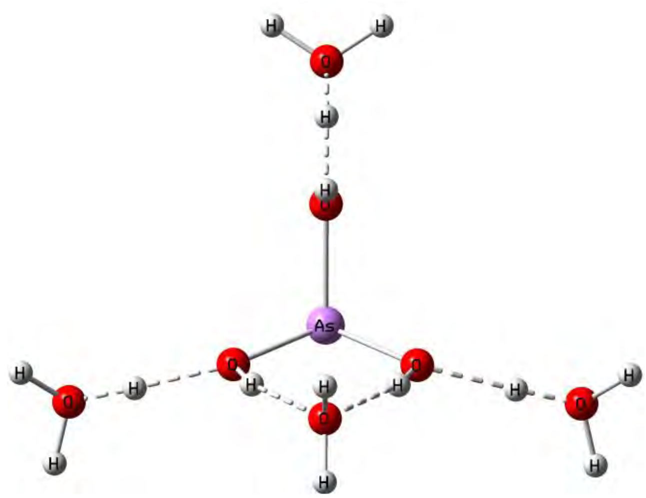
Figure 7f. As^{+3} $7(H_2O)$

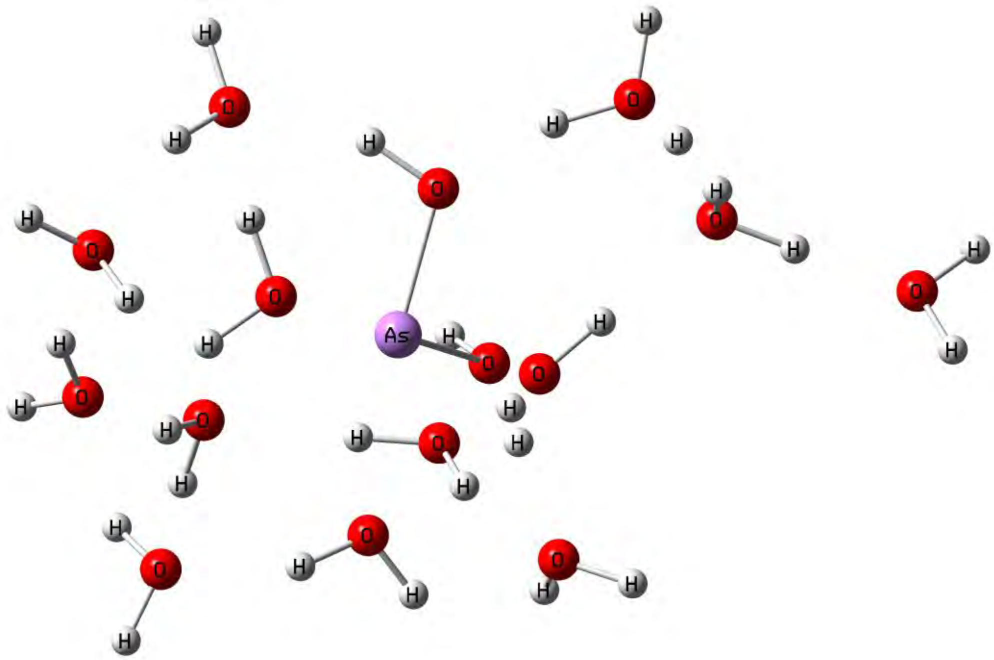

Figure 7g. As^{+3} 15(H_2O)

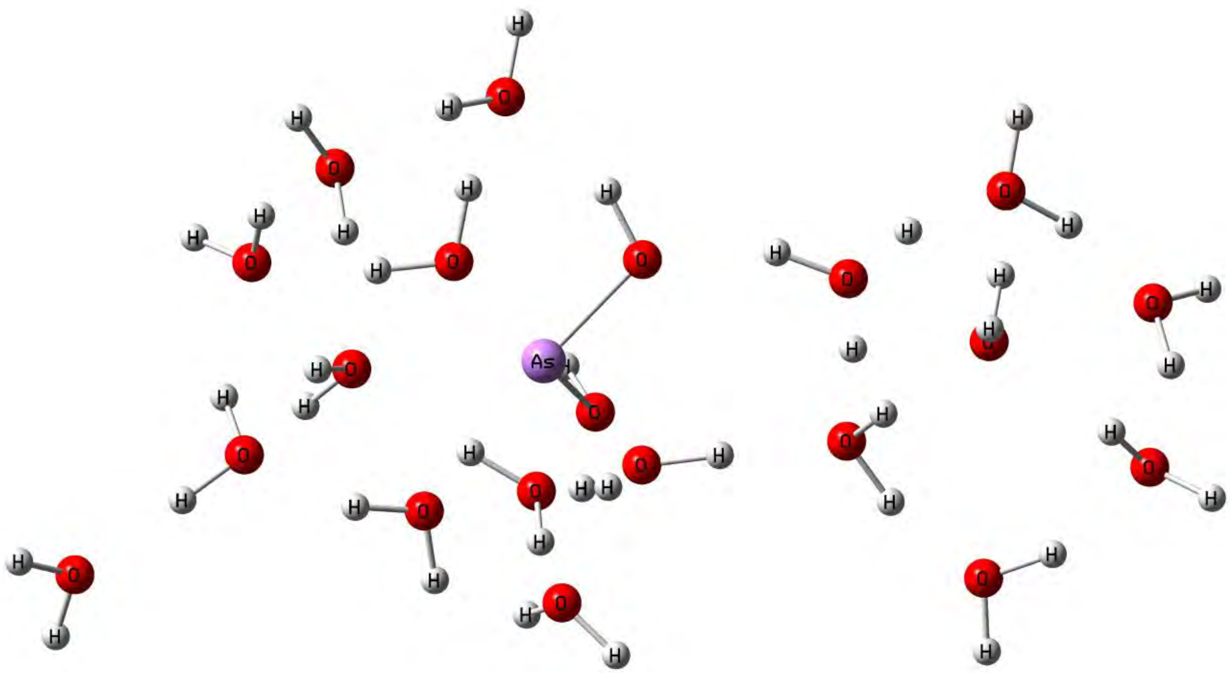

Figure 7h. As^{+3} 20(H_2O)

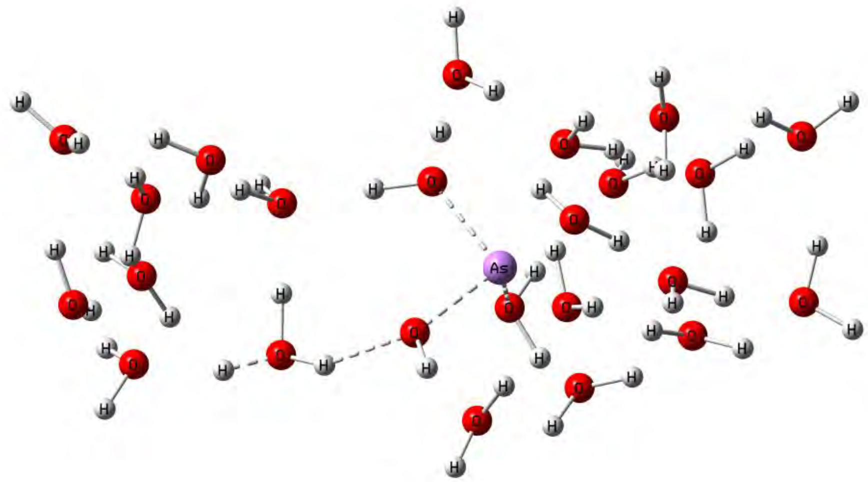

Figure 7i. As^{+3} $24(H_2O)$

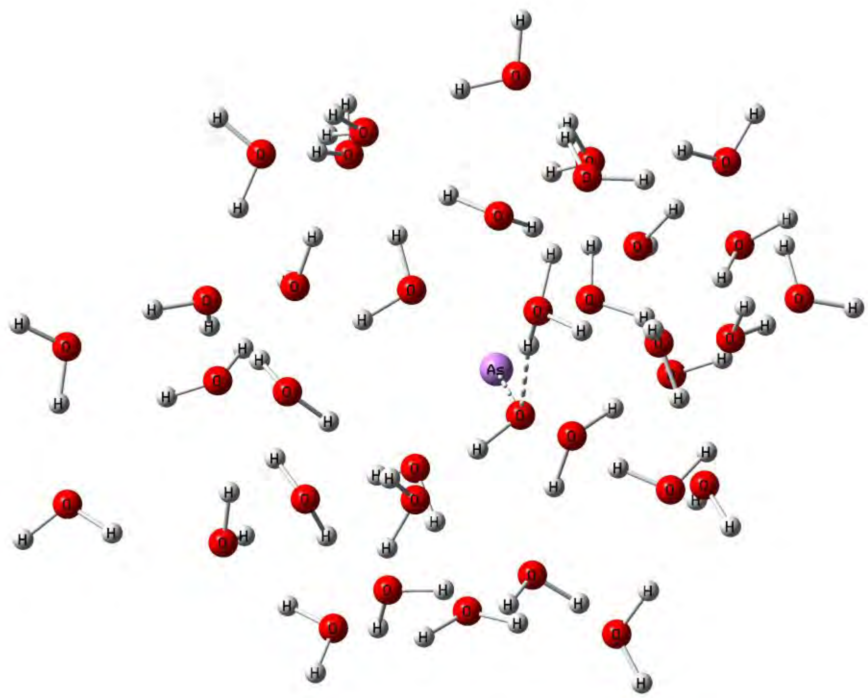

Figure 7j. As^{+3} $36(H_2O)$

Figure 7. Molecular geometries of As-H_2O complexes consisting of 2, 3, 4, 5, 6, 7, 15, 20, 24 and 36 water molecules, without water background.

Table 1. DFT calculated IR spectra for As-H_2O complexes consisting of 2, 3, 4, 5, 6, 7, 15, 20, 24 and 36 water molecules, without water background.

As^{+3} $2(H_2O)$

	Freq	Intensity
1	121.9329	0.0001
2	215.1462	9.545
3	290.8229	4.834
4	539.4944	35.2011
5	543.601	8.3828
6	673.0188	0.0022
7	721.7363	972.4701
8	821.0153	35.06
9	913.8271	81.0759
10	1676.8116	252.1859
11	1700.9889	116.032
12	3143.3518	1863.1696
13	3179.3958	1.5924
14	3232.6057	2.5087
15	3263.1218	1301.0389

As^{+3} $3(H_2O)$

	Freq	Intensity
1	118.8541	1.4453
2	124.7436	1.6233
3	201.5883	0.4904
4	208.4877	0.5273
5	209.9644	0.3490
6	361.6805	13.3450
7	449.6273	13.1701
8	452.0681	13.8033
9	498.5024	23.5960
10	571.5035	379.2382
11	626.7154	404.9844
12	627.2440	409.1182
13	828.0772	36.1948
14	829.3079	36.3902
15	863.5787	113.7884
16	1688.3257	173.3072
17	1688.3903	173.8160
18	1698.4294	58.2587
19	3366.9517	989.4841
20	3367.5376	989.5836

21	3399.7505	11.0189
22	3450.5696	287.8543
23	3451.0181	285.7238
24	3455.5249	906.5205

As^{+3} $4(H_2O)$

	Freq	Intensity
1	52.1709	0.0001
2	102.4299	0.7428
3	132.6806	1.6051
4	156.5802	0.0000
5	187.1399	2.1078
6	201.4429	1.3652
7	268.7141	0.6349
8	302.6066	11.1123
9	340.4676	104.6391
10	360.1412	1.4160
11	364.9940	0.0064
12	418.6682	7.1084
13	470.1066	10.0995
14	523.5901	3.3346
15	552.7140	491.3406
16	585.6903	0.0024
17	623.0650	937.5610
18	694.5346	3.6641
19	753.7066	205.8039
20	807.1002	0.0001
21	845.3121	133.8603
22	1696.0620	32.8934
23	1699.9362	234.6379
24	1719.5782	201.0074
25	1732.3770	7.9408
26	3497.8694	821.6705
27	3507.4446	194.3746
28	3524.2930	928.1411
29	3540.8145	0.2862
30	3573.5859	0.8973
31	3575.5718	693.1871
32	3598.8228	93.6955
33	3599.9368	709.8573

$As^{+3}\ 5(H_2O)$

	Freq	Intensity		Freq	Intensity
1	80.2462	0.6823	22	621.8316	13.8676
2	114.9133	6.3670	23	671.3808	1.3023
3	118.4635	0.0100	24	701.5650	16.7432
4	121.8905	3.6179	25	702.5217	271.3480
5	167.8491	1.1586	26	714.7262	222.9261
6	192.1586	1.1263	27	803.8887	95.8138
7	196.3583	5.3810	28	1630.9944	147.5339
8	200.7035	0.0000	29	1711.8732	157.5089
9	261.1971	5.3955	30	1714.1667	2.3067
10	296.4759	18.5600	31	1717.8260	202.0065
11	302.0874	32.4256	32	1723.6833	10.7513
12	309.2292	0.0025	33	3538.7717	381.7818
13	318.9975	2.1914	34	3587.3596	745.3990
14	327.5310	8.4687	35	3589.7039	1.2957
15	349.9291	0.2218	36	3592.5466	825.1451
16	465.4569	3.1030	37	3607.2654	17.7627
17	494.5114	336.6910	38	3631.8557	319.1275
18	517.8453	0.0046	39	3667.9380	0.0154
19	546.6506	0.0320	40	3668.5420	543.5193
20	547.6634	752.0324	41	3670.7732	29.3654
21	610.8941	434.7337	42	3671.7544	582.5576

$As^{+3}\ 6(H_2O)$

	Freq	Intensity		Freq	Intensity
1	33.5832	2.4531	27	495.8096	545.4608
2	36.3659	2.4223	28	625.8098	0.0000
3	38.1842	2.3875	29	626.4416	0.0000
4	90.9403	5.3733	30	627.4189	0.0000
5	91.5390	5.2511	31	630.4267	346.9003
6	92.1796	5.1072	32	631.5261	350.8729
7	93.6864	0.0000	33	632.4858	342.7031
8	94.5223	0.0000	34	1696.3207	133.7439
9	95.4602	0.0000	35	1696.4259	133.7909
10	220.6121	0.0177	36	1697.2426	133.4885
11	223.6503	0.0204	37	1700.9852	0.0000
12	273.2994	26.4986	38	1701.8242	0.0000
13	274.8800	25.8155	39	1714.6353	0.0000
14	275.9145	25.5428	40	3636.2222	631.3134
15	298.3789	0.0000	41	3636.2832	630.6878
16	300.4626	0.0000	42	3636.3716	631.1205

17	300.8256	0.0000	43	3636.6255	0.0000
18	301.5099	0.0000	44	3636.7244	0.0000
19	301.6427	0.0000	45	3652.6226	0.0000
20	379.1797	0.0000	46	3722.9109	0.0000
21	438.1058	0.0802	47	3723.0183	0.0000
22	477.3677	0.0000	48	3723.1235	0.0000
23	478.7521	0.0000	49	3723.3323	494.5581
24	479.2849	0.0000	50	3723.4404	494.1480
25	494.3228	540.4916	51	3723.5457	494.7417
26	495.0788	548.5722			

As^{+3} $7(H_2O)$

	Freq	Intensity		Freq	Intensity
1	27.2946	0.1178	31	643.5433	177.1789
2	27.3586	2.5145	32	779.2277	38.4059
3	67.2984	29.3713	33	876.9619	114.9147
4	68.2261	17.8607	34	915.4143	265.9611
5	71.7440	9.2266	35	955.3291	0.3359
6	88.5915	1.8976	36	996.7834	411.2122
7	111.4369	22.4966	37	1179.3818	215.0447
8	125.0566	4.2461	38	1257.2511	276.3503
9	134.9420	81.4700	39	1376.0216	32.5341
10	156.9979	29.1986	40	1717.5659	17.0812
11	160.6624	18.3096	41	1720.6215	3.5713
12	172.4638	19.2064	42	1723.0979	4.6110
13	191.5017	0.4809	43	1725.6124	148.4842
14	194.2005	146.1466	44	1727.9495	96.9235
15	225.1129	21.8218	45	1728.3690	23.1800
16	283.7962	374.8981	46	1749.8008	127.5055
17	331.8968	88.3227	47	2527.5771	5739.2778
18	331.9417	0.4480	48	2570.1477	1408.5431
19	388.4761	8.3252	49	2669.2229	2247.4839
20	401.2909	54.2188	50	3273.4978	16.2750
21	439.0588	10.6914	51	3366.0959	1473.8654
22	440.2347	20.2706	52	3666.2578	362.7159
23	448.1105	1.2816	53	3667.5322	433.9402
24	453.4723	12.0943	54	3669.8171	9.1475
25	496.4685	42.8844	55	3720.0549	49.2258
26	498.9471	124.4539	56	3722.9688	112.4754
27	503.9446	777.3667	57	3741.6587	308.5476
28	529.0278	235.2419	58	3744.2410	150.5281
29	557.4718	378.6260	59	3744.6062	657.5589

30	613.2416	2.4568	60	3789.7961	181.1047

As^{+3} 15(H_2O)

	Freq	Intensity		Freq	Intensity		Freq	Intensity		Freq	Intensity
1	21.7748	0.5885	34	254.3414	36.7957	67	668.2455	201.5173	100	1775.2606	136.3393
2	31.4092	1.1939	35	258.8140	4.5919	68	673.8940	50.0432	101	1796.3989	98.7515
3	36.7232	0.8972	36	269.3612	154.6916	69	682.2879	128.0455	102	1828.2961	247.6664
4	42.9863	3.8355	37	282.5832	64.1988	70	706.8125	211.9441	103	2231.3513	2260.7878
5	48.9529	0.6487	38	325.0440	105.4648	71	762.7829	41.2636	104	2606.4470	2484.9001
6	54.2563	0.2469	39	333.8670	72.1568	72	767.3516	130.7586	105	2730.4927	1828.6000
7	57.2796	3.8245	40	346.2043	17.5702	73	777.2997	17.4902	106	2899.8030	1999.5959
8	61.8409	4.0321	41	381.8454	56.2926	74	813.2959	80.8607	107	2962.2466	1807.9385
9	68.9406	0.9217	42	390.4701	319.2003	75	845.1943	121.5948	108	3250.6243	386.0734
10	74.1299	0.9022	43	398.7773	56.1504	76	870.6986	485.8610	109	3274.1174	1022.9997
11	81.1355	2.0046	44	401.8239	30.7786	77	883.5528	137.0674	110	3427.7214	1079.8733
12	90.8351	1.4853	45	419.4186	13.4093	78	897.1777	309.5571	111	3429.0298	252.3512
13	95.3222	0.2493	46	429.9523	49.9352	79	924.0028	106.5853	112	3461.3142	228.9977
14	96.6173	1.9490	47	436.8747	32.1679	80	981.3914	116.4194	113	3466.6853	442.6014
15	106.4722	0.2118	48	440.8828	92.8036	81	1026.3170	209.6005	114	3496.4478	1002.6121
16	120.7118	0.6761	49	446.3902	10.4322	82	1030.0234	107.6784	115	3521.0381	1004.9267
17	121.9981	5.2033	50	455.9313	10.2093	83	1092.4189	129.0954	116	3539.7893	520.6955
18	127.2531	1.6855	51	466.5205	8.6734	84	1128.9388	219.5871	117	3548.8220	97.3483
19	138.4957	4.1136	52	490.3304	145.6285	85	1179.2942	106.3070	118	3575.0962	223.3816
20	145.2705	8.2402	53	499.6628	22.1216	86	1289.3363	215.4610	119	3680.3894	162.9019
21	152.1417	6.0175	54	504.5464	7.6265	87	1336.6538	92.5618	120	3744.0425	113.6093
22	159.9338	8.5863	55	531.5247	33.7619	88	1616.1250	103.5525	121	3769.5068	90.3258
23	164.3226	8.6670	56	535.2122	43.4069	89	1695.3168	42.5751	122	3771.4500	147.9481
24	168.0756	3.1883	57	544.7838	109.3062	90	1704.6752	101.8911	123	3774.6914	207.9796
25	173.0969	2.3862	58	550.8257	6.3721	91	1708.7004	112.4074	124	3782.1101	79.5982
26	182.1701	49.1190	59	574.3355	25.0623	92	1721.4930	34.9803	125	3787.1165	195.9538
27	195.2640	4.4089	60	581.2824	12.6718	93	1727.9373	186.2910	126	3790.7097	125.4452
28	200.1730	20.1165	61	590.5375	295.8192	94	1732.5436	73.6251	127	3792.9971	143.6032
29	212.8958	16.9500	62	592.5421	100.0730	95	1733.4402	208.2131	128	3801.8462	201.8807
30	220.7674	17.7531	63	600.1362	172.8089	96	1734.3087	57.2684	129	3804.7239	120.5247
31	231.6244	2.8179	64	612.5311	36.4037	97	1749.0583	14.3863	130	3825.7876	153.8602
32	235.7267	44.6643	65	621.4504	83.3461	98	1751.4373	73.6222	131	3837.3120	159.0305
33	242.0704	19.8718	66	646.8388	234.9585	99	1754.1760	169.0490	132	3857.9937	149.3164

As^{+3} 20(H_2O)

	Freq	Intensity		Freq	Intensity		Freq	Intensity		Freq	Intensity
1	15.6806	0.2777	46	243.0471	112.8256	91	689.3722	186.9725	136	1809.2108	160.0324
2	17.5745	1.0813	47	248.2719	19.5868	92	690.6630	65.3766	137	1892.5400	265.1630
3	25.5442	0.8881	48	260.5594	26.5164	93	717.2634	66.9354	138	2450.1514	2938.0127
4	37.2651	1.2120	49	266.4231	36.8865	94	744.5807	58.0799	139	2709.3264	926.4713
5	39.9414	0.0586	50	279.4226	177.4646	95	749.7878	78.0012	140	2784.3098	2028.8992
6	42.6652	3.5092	51	289.8252	77.5219	96	757.6064	187.5528	141	2812.9050	1739.9822
7	44.0597	0.3338	52	312.4328	99.4431	97	767.4091	21.3843	142	2892.4663	3835.3826
8	46.3815	0.7142	53	315.4920	78.9841	98	801.8222	105.3410	143	2982.3284	1437.3170
9	50.1288	1.6963	54	329.8141	26.0716	99	807.2735	98.7117	144	3059.3401	514.2514
10	55.4810	0.4877	55	340.3055	31.6741	100	824.3420	80.8786	145	3243.2114	1155.6260
11	57.0101	1.4108	56	340.6055	285.4521	101	862.3109	273.0102	146	3306.3228	1098.3239
12	63.5399	0.5451	57	350.8330	58.1556	102	865.3542	443.6188	147	3313.7449	509.2757
13	65.4262	1.0320	58	364.1090	24.1617	103	884.3472	45.4942	148	3333.6138	1360.2769
14	72.2291	0.5342	59	367.6239	60.0290	104	888.8495	101.2619	149	3402.3372	1016.2563
15	74.0037	1.2504	60	374.9191	19.2643	105	927.8866	225.5117	150	3408.7300	96.9728
16	77.9704	0.7586	61	401.3971	9.0547	106	970.7422	152.9288	151	3443.9019	825.6947
17	82.3388	2.1081	62	406.6597	23.8458	107	979.7673	70.9100	152	3452.3799	342.6637
18	86.2981	0.6410	63	418.5089	24.9009	108	1002.1777	152.4649	153	3491.9492	502.7393
19	94.4751	0.8562	64	421.1097	6.2261	109	1018.6153	183.7240	154	3510.4771	258.1131
20	96.7237	2.7937	65	428.8289	5.8890	110	1030.0323	213.3059	155	3536.7275	622.3220
21	98.6239	1.3039	66	433.2990	13.2097	111	1078.7467	147.6121	156	3556.2227	328.5725
22	109.5115	9.6760	67	439.6963	0.5160	112	1088.1298	122.2360	157	3578.5632	29.2012
23	117.7787	2.5487	68	453.2049	148.1174	113	1110.7247	153.0397	158	3579.6870	610.5163
24	119.5842	1.7055	69	475.5166	67.6310	114	1138.0688	153.9725	159	3598.3699	652.7500
25	130.3860	13.0760	70	485.6645	13.3885	115	1208.5477	94.7050	160	3644.5474	203.0024
26	132.8400	16.4563	71	489.1872	4.7595	116	1298.8879	169.3891	161	3648.5437	293.1607
27	140.2085	2.7582	72	505.6554	66.5270	117	1342.7242	335.5362	162	3650.2114	215.6688
28	143.2224	6.0806	73	513.8757	118.1147	118	1696.2584	131.4459	163	3754.7839	78.6404
29	153.5226	10.4535	74	514.6788	19.0399	119	1700.9406	33.4376	164	3781.4890	28.3806
30	156.5511	2.0349	75	517.0840	51.2268	120	1703.6373	87.5662	165	3793.0073	59.5699
31	159.0698	11.6021	76	525.2366	135.4170	121	1704.1772	58.8525	166	3798.3184	141.4747
32	165.4012	1.7470	77	542.7168	39.7939	122	1713.5968	61.0891	167	3807.9841	140.7067
33	171.8201	9.9842	78	565.7089	180.7170	123	1719.0287	39.3810	168	3809.4143	120.5661
34	173.7443	10.9547	79	573.4206	68.2040	124	1723.4664	191.9136	169	3812.1904	93.1774
35	185.5182	27.8598	80	579.8313	152.4841	125	1730.6964	119.8314	170	3815.5549	146.6635
36	188.7656	2.2012	81	586.9724	120.7701	126	1731.5750	172.7169	171	3817.6216	148.2150
37	199.4447	11.4062	82	604.8421	90.8676	127	1733.6876	184.6938	172	3818.4001	124.1258
38	202.7727	12.0789	83	608.8448	115.8938	128	1733.7979	18.2454	173	3839.9158	138.7402
39	205.7082	20.5878	84	611.7298	161.3786	129	1747.4985	17.9780	174	3847.6729	141.4337
40	218.3222	72.7580	85	615.6924	32.2587	130	1748.2578	57.8275	175	3853.8706	165.4266

41	221.9663	49.9775	86	628.9331	40.0545	131	1755.4734	102.4719	176	3860.8557	104.6106
42	225.2913	24.5628	87	643.2077	107.8900	132	1756.8550	49.9637	177	3874.4797	115.0030
43	228.3043	18.7493	88	657.8812	76.4540	133	1767.1278	2.6615			
44	233.4156	34.6285	89	665.2930	383.2071	134	1773.0446	138.2307			
45	238.9702	10.5474	90	679.0679	147.2139	135	1794.8252	112.1142			

As^{+3} 24(H_2O)

	Freq	Intensity		Freq	Intensity		Freq	Intensity		Freq	Intensity
1	13.3796	0.0854	55	257.7064	74.8738	109	717.7892	133.4267	163	1810.1610	11.1438
2	17.6168	0.8237	56	267.6863	66.4627	110	723.2850	77.5957	164	1835.3695	76.5422
3	26.5292	1.3699	57	272.1475	72.4900	111	731.0013	104.4801	165	1896.0793	319.9697
4	35.1107	2.1236	58	284.7564	12.4950	112	738.5616	71.9511	166	2371.5522	2077.7690
5	39.3614	4.1128	59	285.3606	58.6485	113	761.9628	30.0401	167	2563.3904	2666.5713
6	40.8185	0.0716	60	304.0190	52.8147	114	763.1367	95.3007	168	2589.0476	2152.8103
7	45.1282	0.0013	61	311.5912	13.4233	115	782.0099	408.2374	169	2674.6677	2435.2871
8	53.4435	0.0870	62	321.3554	5.8604	116	787.7006	237.8839	170	2845.2241	2095.0193
9	55.9359	0.2173	63	323.5086	26.3097	117	814.8787	7.0099	171	2908.2278	1798.5798
10	57.1979	5.2488	64	328.3089	33.0984	118	818.4987	103.0777	172	2947.1218	1247.2991
11	61.0336	0.5329	65	332.8359	101.9951	119	820.3943	106.0732	173	3190.8496	766.9843
12	66.1310	3.5503	66	338.2757	11.9913	120	825.8800	95.9504	174	3314.2234	403.6730
13	67.9573	1.3455	67	357.2548	75.4385	121	836.5977	62.9654	175	3358.0659	345.8841
14	72.1354	0.6409	68	369.5386	9.9281	122	868.8837	227.2453	176	3380.5298	424.7529
15	75.7471	0.5544	69	378.0419	24.5615	123	880.8064	57.9049	177	3397.3467	711.9899
16	79.1900	1.6354	70	387.7336	42.7608	124	888.7847	160.5753	178	3399.3503	492.1994
17	87.1607	2.6244	71	408.3910	2.4197	125	899.0733	186.5709	179	3425.6626	1157.0211
18	88.3064	0.7411	72	411.7740	6.5087	126	922.3788	85.5562	180	3437.5515	599.1726
19	95.7868	5.5286	73	413.0471	22.9742	127	931.2334	166.3924	181	3451.8508	981.3995
20	97.1800	1.0137	74	421.8634	16.3676	128	936.7377	291.5160	182	3465.0676	593.1556
21	101.5430	1.9114	75	427.2084	16.3944	129	956.0651	646.7192	183	3478.1790	234.1018
22	103.5540	0.3754	76	428.7655	30.7109	130	973.4122	214.9064	184	3489.6550	420.2721
23	105.1430	0.7668	77	441.4528	0.8771	131	995.3453	224.4277	185	3505.1084	791.9524
24	110.1684	3.7899	78	442.7459	28.1847	132	1030.4266	149.6150	186	3512.8442	329.3309
25	116.7365	3.5031	79	445.1599	21.4466	133	1044.8326	152.6562	187	3525.8008	461.1841
26	123.5580	10.5787	80	451.6979	71.6999	134	1061.5341	30.4028	188	3542.1299	534.6897
27	127.1487	9.2009	81	456.8710	72.3549	135	1076.1993	166.0209	189	3580.9541	301.3779
28	133.9465	3.3671	82	486.6558	6.4983	136	1142.5811	138.4159	190	3583.8848	107.0818
29	134.4247	26.5519	83	500.0794	155.3741	137	1147.2362	52.7693	191	3594.0171	176.6473
30	138.8358	0.4051	84	505.1557	52.0589	138	1199.9058	118.3565	192	3599.4021	688.6100
31	140.6668	15.4262	85	506.7812	145.3674	139	1264.1467	89.1320	193	3610.4700	503.9652
32	146.7824	30.9704	86	513.2432	41.7950	140	1349.2258	177.1215	194	3610.7803	146.3389
33	148.3793	2.3766	87	520.7268	36.1220	141	1397.2227	310.9044	195	3629.3296	282.6623
34	152.9513	3.5080	88	543.4525	14.5623	142	1695.8214	143.8182	196	3649.6982	256.6672

35	160.5720	2.4907	89	548.9702	51.7635	143	1699.5635	52.1994	197	3667.4749	322.3621
36	166.6442	4.2087	90	556.4452	40.2195	144	1702.4572	4.9542	198	3698.2168	608.0537
37	170.4324	15.4718	91	567.5352	169.9506	145	1713.2198	97.2770	199	3699.4788	289.1845
38	173.0420	12.4386	92	570.0769	11.5660	146	1718.6533	124.0458	200	3756.5469	14.3984
39	177.1298	0.5124	93	578.8842	121.8426	147	1723.2638	111.0600	201	3756.9954	73.3964
40	183.3235	12.7011	94	581.2336	160.7122	148	1726.0597	73.9686	202	3812.4109	15.3463
41	186.1079	0.4097	95	584.0515	118.8026	149	1726.5970	64.8864	203	3813.5835	138.0585
42	193.8359	4.4604	96	591.9546	1.2093	150	1727.5269	136.5013	204	3813.7109	136.8984
43	195.5730	10.4795	97	599.3642	221.3279	151	1728.3647	104.9887	205	3816.3782	214.4808
44	200.2277	4.2868	98	609.3380	152.9386	152	1731.1390	135.1185	206	3816.5823	117.5129
45	202.1215	15.1500	99	613.1743	3.4643	153	1731.7668	119.1964	207	3818.3606	67.4201
46	215.1533	30.1959	100	618.8294	98.9268	154	1734.2784	21.9091	208	3821.8579	117.3209
47	219.0526	6.3705	101	625.8869	65.4961	155	1742.7740	70.1892	209	3826.2063	119.8921
48	223.3044	9.6841	102	645.9845	158.8204	156	1760.1848	93.2517	210	3829.7954	148.1452
49	225.7606	3.0717	103	650.4483	306.0678	157	1766.1995	158.9413	211	3841.4807	108.2093
50	228.1692	21.6016	104	655.0595	16.3569	158	1769.2115	88.2904	212	3843.7766	136.4028
51	236.7416	7.3496	105	664.6500	63.2705	159	1782.9594	194.9591	213	3850.5500	133.0775
52	237.7299	23.5300	106	671.9087	573.6432	160	1796.6754	31.4666			
53	248.7955	15.4514	107	690.2520	96.5381	161	1802.0203	194.4309			
54	253.1559	13.1855	108	704.7054	14.7984	162	1808.9791	181.9889			

As^{+3} 36(H_2O)

	Freq	Intensity		Freq	Intensity		Freq	Intensity		Freq	Intensity
1	21.1945	0.0392	82	253.3427	7.4271	163	730.9009	25.9001	244	1790.8651	27.6709
2	25.2446	0.2351	83	255.5532	35.7290	164	743.5515	72.0243	245	1792.5160	26.7398
3	30.5809	0.1451	84	259.1662	10.6871	165	749.8541	145.2969	246	1805.8381	15.1820
4	33.3375	0.1537	85	260.7739	84.8103	166	758.0769	142.3680	247	1809.0867	163.1361
5	33.7765	0.4638	86	263.6497	14.0207	167	759.7164	64.1597	248	1814.8054	83.0804
6	35.7093	0.1697	87	272.5931	118.1094	168	765.4753	73.9334	249	1880.9760	172.3666
7	38.7694	0.8008	88	273.7149	20.8322	169	775.9351	143.4215	250	2298.3728	2812.5955
8	39.1834	0.4264	89	274.9292	75.5785	170	782.5242	149.9557	251	2392.7859	2132.7002
9	41.3978	1.9176	90	279.5925	22.0260	171	788.9273	119.6760	252	2811.7830	3290.0259
10	42.9967	0.3833	91	287.2500	14.8235	172	789.9868	59.0005	253	2830.2561	298.9835
11	46.5131	1.4204	92	289.3551	16.2432	173	797.3202	140.8847	254	2883.1125	2881.0564
12	47.6857	2.6473	93	291.3328	52.5536	174	798.6889	354.7419	255	2901.5554	1538.8444
13	50.6973	0.8038	94	298.4433	118.4620	175	811.6470	89.9969	256	3013.6267	611.5072
14	53.9060	1.1348	95	304.3216	28.0646	176	818.4235	345.1515	257	3041.1252	483.3280
15	54.7472	1.8216	96	305.7489	70.2106	177	831.7926	85.2818	258	3064.6963	1729.6259
16	56.6067	0.2788	97	312.0739	28.9011	178	835.7442	348.5915	259	3096.2935	2099.7771
17	58.6857	0.4126	98	317.2798	80.1969	179	841.5125	70.1412	260	3104.3711	1626.4127
18	63.6717	3.2979	99	319.8781	75.8676	180	843.2790	121.7791	261	3168.9231	834.1947
19	65.3344	0.6357	100	332.4293	62.8634	181	850.4600	50.7982	262	3201.2251	945.2572

20	67.3515	1.3120	101	336.8376	12.2480	182	854.3214	23.8436	263	3280.4402	1366.7618
21	69.4085	0.2658	102	347.3063	19.8409	183	864.2537	49.8662	264	3324.6377	739.9585
22	70.5468	1.3152	103	370.9341	43.2646	184	871.4430	201.0522	265	3337.8677	468.4179
23	72.8416	2.0328	104	372.4847	36.0885	185	882.4036	304.1534	266	3345.5999	1167.7567
24	74.5276	0.7518	105	375.6657	7.5479	186	888.2569	20.3933	267	3350.6914	761.6975
25	77.0266	0.1848	106	383.8798	12.6986	187	908.7320	14.0249	268	3364.2666	480.8228
26	78.4312	0.3153	107	385.2386	12.6107	188	915.8900	140.3120	269	3377.1665	799.7071
27	80.6783	0.8476	108	388.0892	24.0008	189	926.2691	45.3952	270	3412.7974	860.8928
28	82.8482	0.7229	109	392.6111	5.6024	190	932.2836	751.3289	271	3420.8115	724.5559
29	83.8999	0.8218	110	394.8710	5.3192	191	946.4199	79.8088	272	3432.0012	317.5394
30	87.2901	1.1114	111	396.7638	33.8102	192	951.5992	175.6645	273	3447.2954	345.4579
31	88.6907	0.8059	112	412.6635	31.7707	193	956.3922	123.2532	274	3451.1096	454.5877
32	93.7821	4.0530	113	419.7995	70.6120	194	976.4851	72.4070	275	3455.1372	466.2496
33	95.4333	3.0692	114	423.3034	35.3173	195	985.8504	136.1778	276	3456.2368	627.4613
34	98.1782	0.6804	115	426.2058	79.8504	196	995.0315	48.5827	277	3461.5408	513.3464
35	100.4267	2.6057	116	430.1048	55.7186	197	1010.1855	24.0455	278	3466.1787	963.7542
36	101.5736	3.7605	117	439.5307	76.5018	198	1018.0413	233.2000	279	3482.4697	616.0438
37	103.6915	2.5066	118	441.9765	32.8934	199	1020.8259	117.0957	280	3490.3423	282.8244
38	107.4941	3.5789	119	446.4105	19.3503	200	1029.0808	270.3748	281	3495.1270	869.9085
39	109.0738	15.5766	120	454.7374	7.7567	201	1077.7521	55.1757	282	3501.7688	766.5783
40	116.0363	1.5588	121	456.0611	22.9670	202	1078.8827	132.8752	283	3505.4592	298.8603
41	117.7585	5.4459	122	462.7791	16.9966	203	1081.9727	150.8751	284	3522.2058	490.1756
42	120.6928	1.0558	123	466.7441	7.6734	204	1093.7926	40.9103	285	3541.2373	1089.0104
43	122.1151	2.1460	124	469.0827	19.0661	205	1103.4928	141.6601	286	3543.5571	56.3347
44	128.3423	5.0369	125	475.1816	45.7670	206	1127.3044	336.5521	287	3546.5403	330.8702
45	131.8387	1.6323	126	477.9818	28.7560	207	1136.2897	97.9282	288	3555.8020	414.3755
46	134.3430	38.9137	127	484.1191	27.7417	208	1160.9965	170.2413	289	3560.6975	428.8538
47	140.3052	9.4220	128	489.8287	61.9781	209	1176.7996	305.4186	290	3566.4214	1113.3698
48	143.5279	12.8061	129	492.0647	17.6707	210	1185.3416	118.7996	291	3570.8408	430.4417
49	145.1253	4.7692	130	509.5014	91.0554	211	1278.1860	109.2598	292	3578.4829	396.7320
50	145.5423	2.7219	131	515.9656	8.0936	212	1290.5867	69.5205	293	3593.0352	752.5378
51	153.2019	12.2694	132	516.9601	46.2784	213	1333.8218	326.4585	294	3597.0901	320.3497
52	157.5749	5.8275	133	523.9105	39.5528	214	1684.8550	7.8860	295	3615.2002	343.1382
53	162.3955	4.1175	134	527.2262	30.5546	215	1688.9547	28.3079	296	3623.5420	178.9618
54	164.5710	2.8935	135	529.2324	115.9746	216	1699.6863	145.6836	297	3638.6567	184.1653
55	168.7538	3.0915	136	540.5267	49.8267	217	1705.0067	63.0248	298	3670.1626	411.1499
56	169.2905	1.5575	137	545.8881	43.1617	218	1706.0767	158.0592	299	3678.0815	242.2075
57	175.5467	3.4489	138	554.5110	99.0643	219	1708.4515	54.2225	300	3681.8384	681.9995
58	177.5591	8.3144	139	557.4026	305.4085	220	1716.0745	5.6116	301	3682.6985	190.6398
59	181.3970	7.9740	140	561.2762	218.9672	221	1719.2037	122.2674	302	3695.5095	370.4041
60	184.1518	24.2177	141	575.2131	23.7857	222	1720.1775	156.3689	303	3807.0330	56.5216
61	186.3473	47.0133	142	586.0448	30.5020	223	1722.2738	44.8801	304	3810.7068	83.5553

62	188.9226	5.7930	143	590.7434	48.5037	224	1724.6034	192.5430	305	3811.7456	108.7834
63	192.4546	57.1469	144	595.8147	312.4825	225	1727.1681	89.2246	306	3812.0974	83.0358
64	195.9459	21.9858	145	600.5397	51.5403	226	1728.8240	210.2996	307	3817.0046	79.8879
65	197.4766	66.8506	146	602.8859	65.8534	227	1732.1735	181.0311	308	3817.7861	84.7713
66	200.4129	15.8660	147	608.3292	32.5591	228	1736.8655	23.7594	309	3819.1836	105.4134
67	202.3675	6.7822	148	612.7506	47.3147	229	1742.8160	98.7875	310	3820.3982	135.3706
68	203.7219	12.0173	149	614.6777	21.4102	230	1745.4949	56.4170	311	3820.8550	95.4335
69	204.9958	93.7583	150	629.6055	271.4542	231	1746.3616	91.5790	312	3821.1941	109.9041
70	208.8729	44.6776	151	636.3116	107.1510	232	1748.0293	59.3741	313	3826.3247	140.3809
71	212.9289	18.0481	152	643.1618	30.1066	233	1749.2411	46.4114	314	3826.3694	68.4109
72	216.1458	117.0692	153	655.1141	90.2810	234	1753.1003	3.8287	315	3846.8372	83.1592
73	220.9400	15.6952	154	660.7387	160.1305	235	1755.1665	56.5913	316	3850.0251	107.5781
74	223.3002	57.3190	155	664.3084	116.6797	236	1757.4418	71.2052	317	3851.4609	121.0092
75	224.4590	113.1921	156	675.4431	100.8008	237	1760.4280	99.6595	318	3854.2466	119.9625
76	229.1303	36.0364	157	682.1953	196.7988	238	1762.9727	18.0400	319	3866.3125	166.4124
77	232.4080	10.9179	158	685.6861	31.2477	239	1765.2482	59.3934	320	3867.1082	96.5297
78	235.7849	18.3671	159	701.9610	7.8401	240	1766.5707	12.8104	321	3868.6436	145.5053
79	236.9076	10.9845	160	709.9515	21.0527	241	1775.5872	75.6657			
80	247.4933	98.9895	161	723.1542	112.0123	242	1782.8850	7.5517			
81	250.2338	32.4292	162	728.3499	45.3831	243	1784.4091	52.5698			

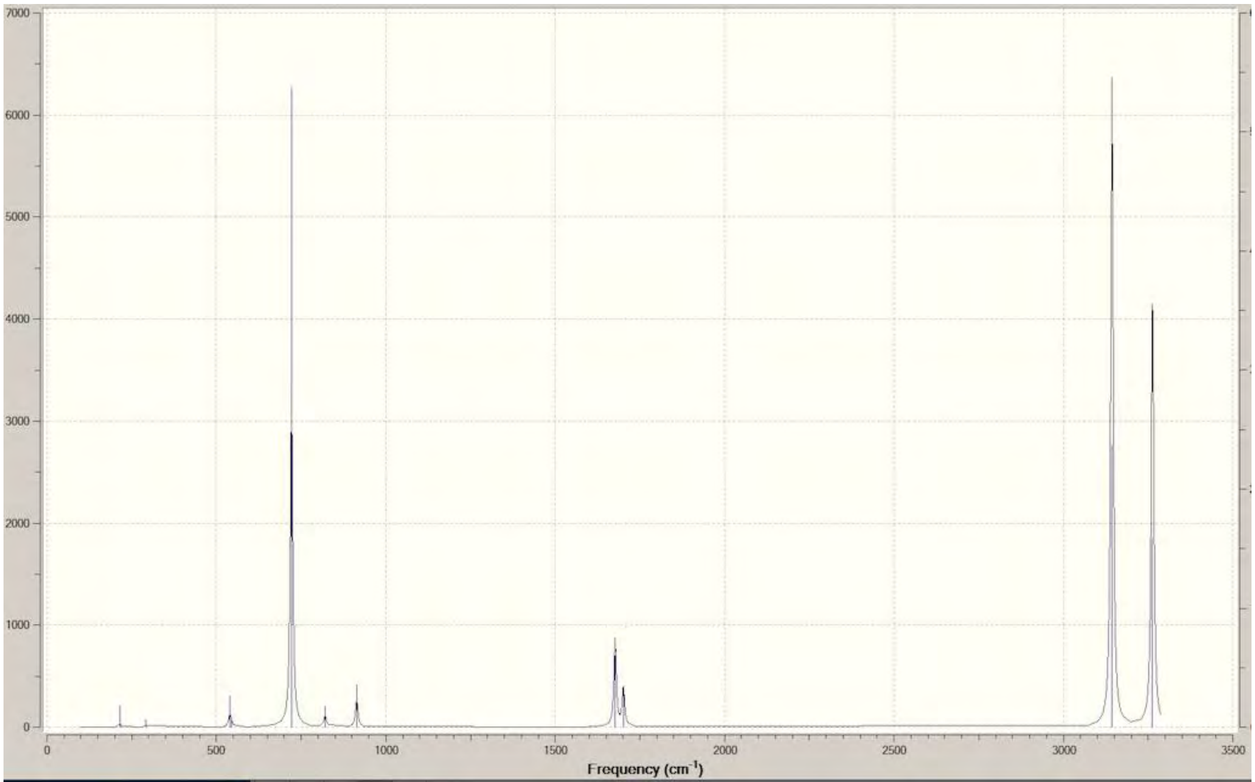

Figure 8a. As^{+3} $2(H_2O)$

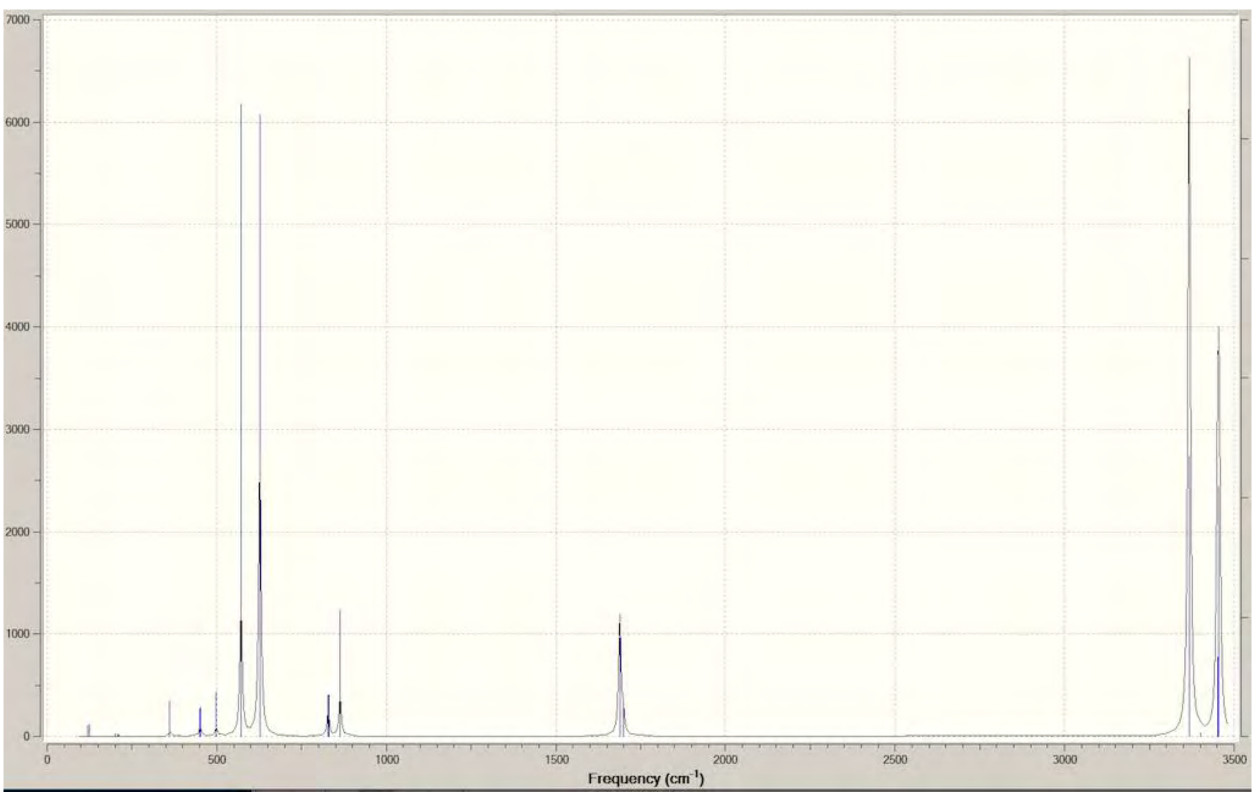

Figure 8b. As^{+3} $3(H_2O)$

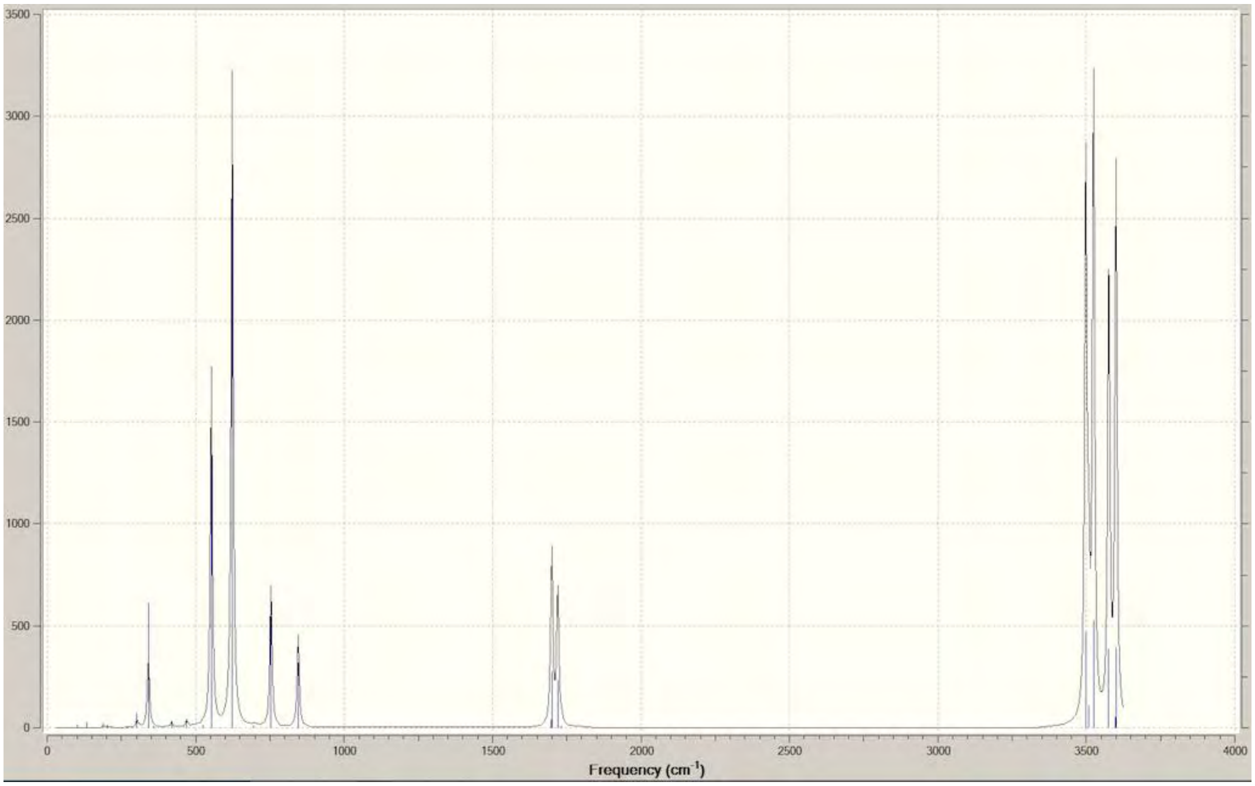

Figure 8c. As^{+3} 4(H_2O)

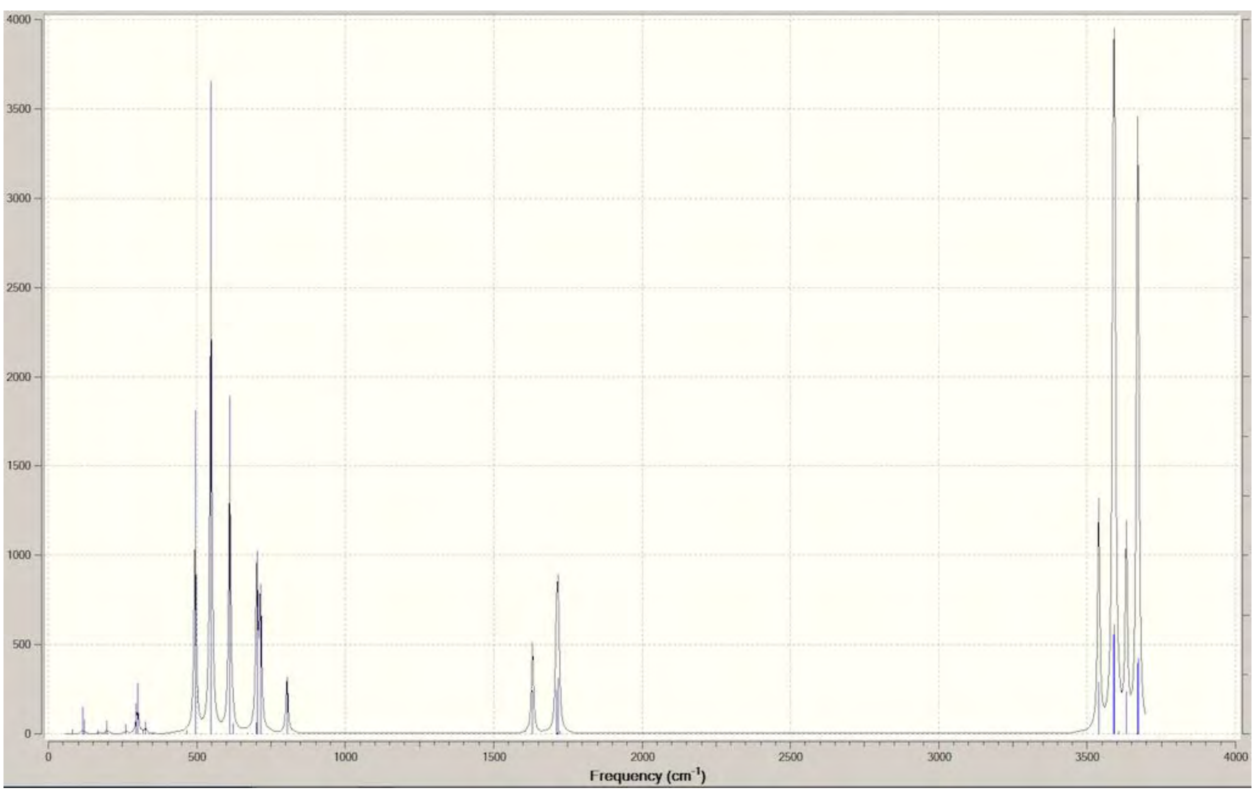

Figure 8d. As^{+3} 5(H_2O)

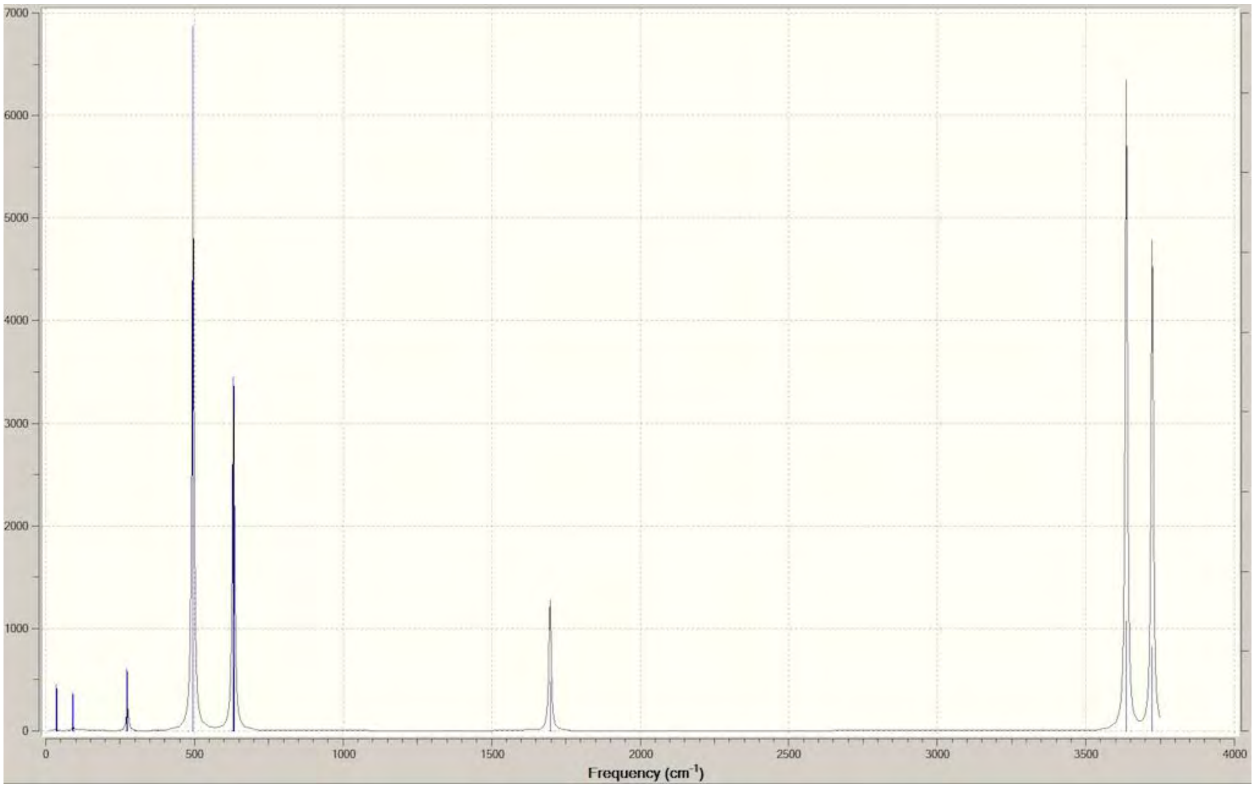

Figure 8e. As^{+3} 6(H_2O)

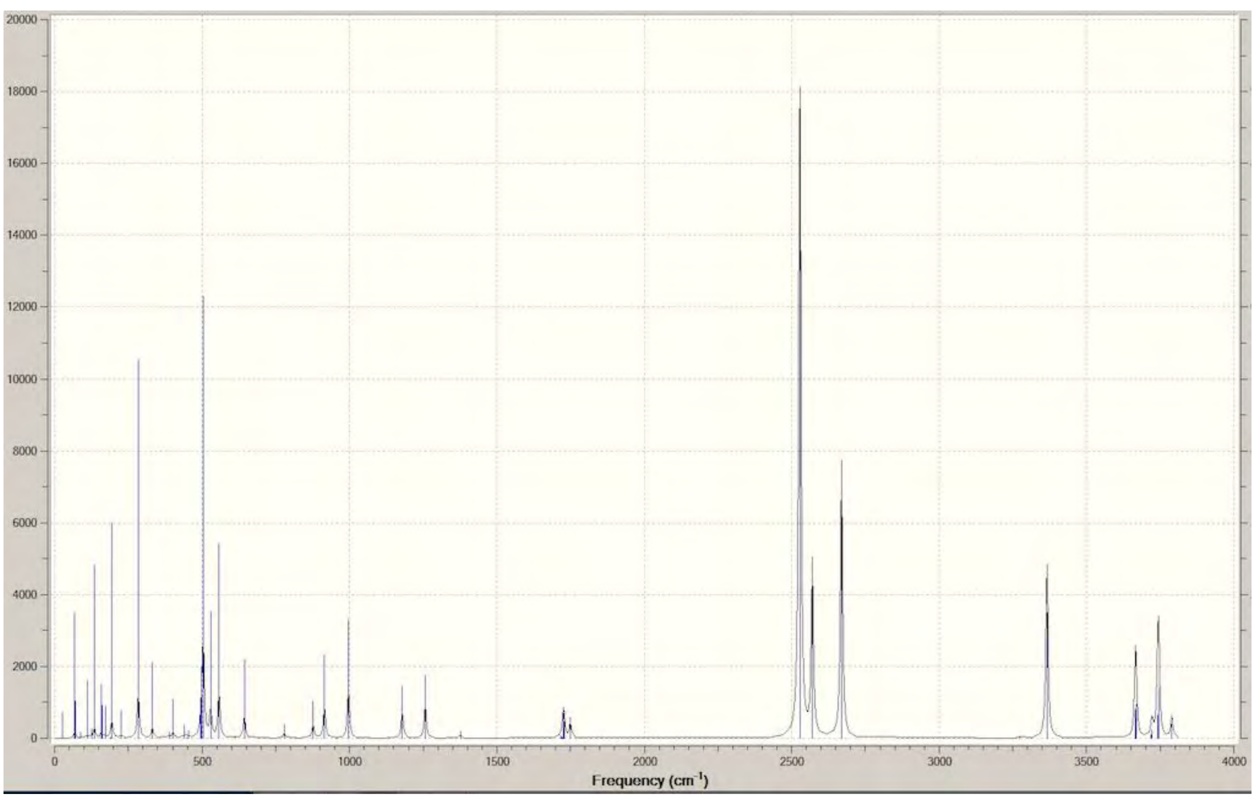

Figure 8f. As^{+3} 7(H_2O)

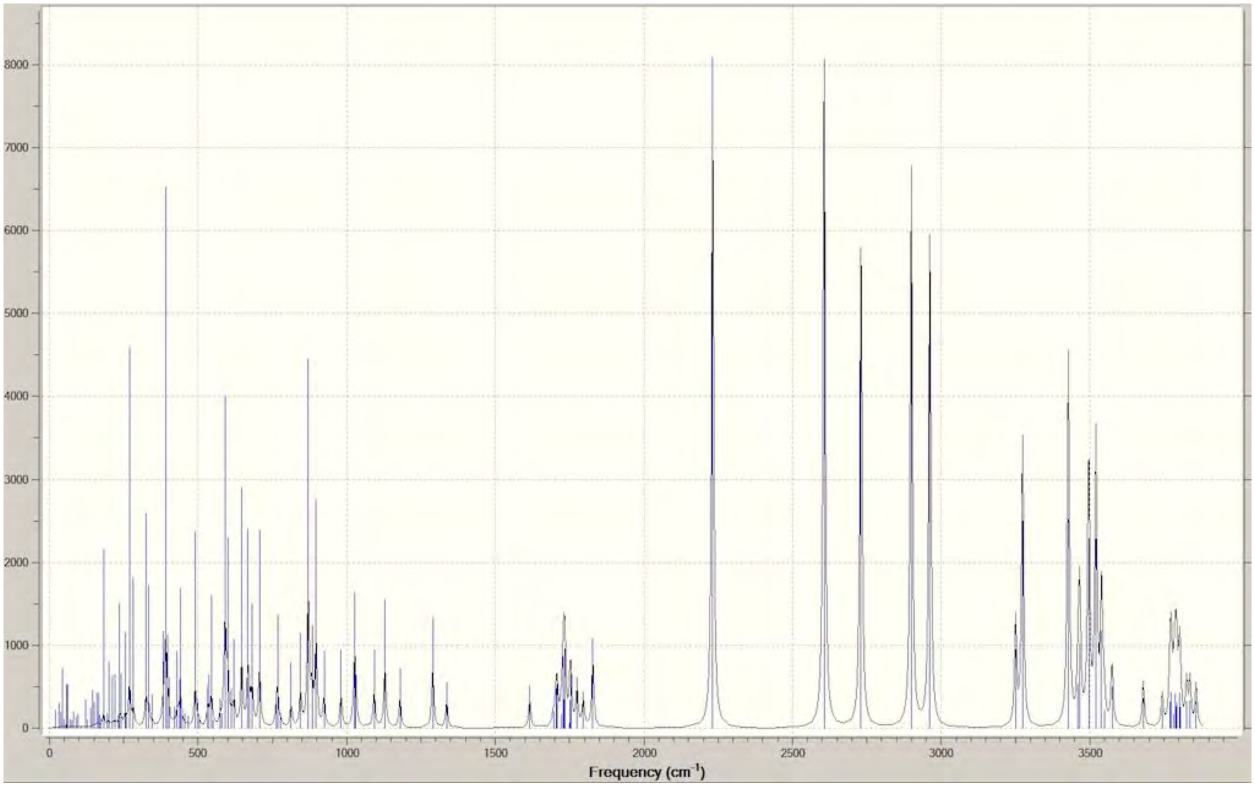

Figure 8g. As^{+3} 15(H_2O)

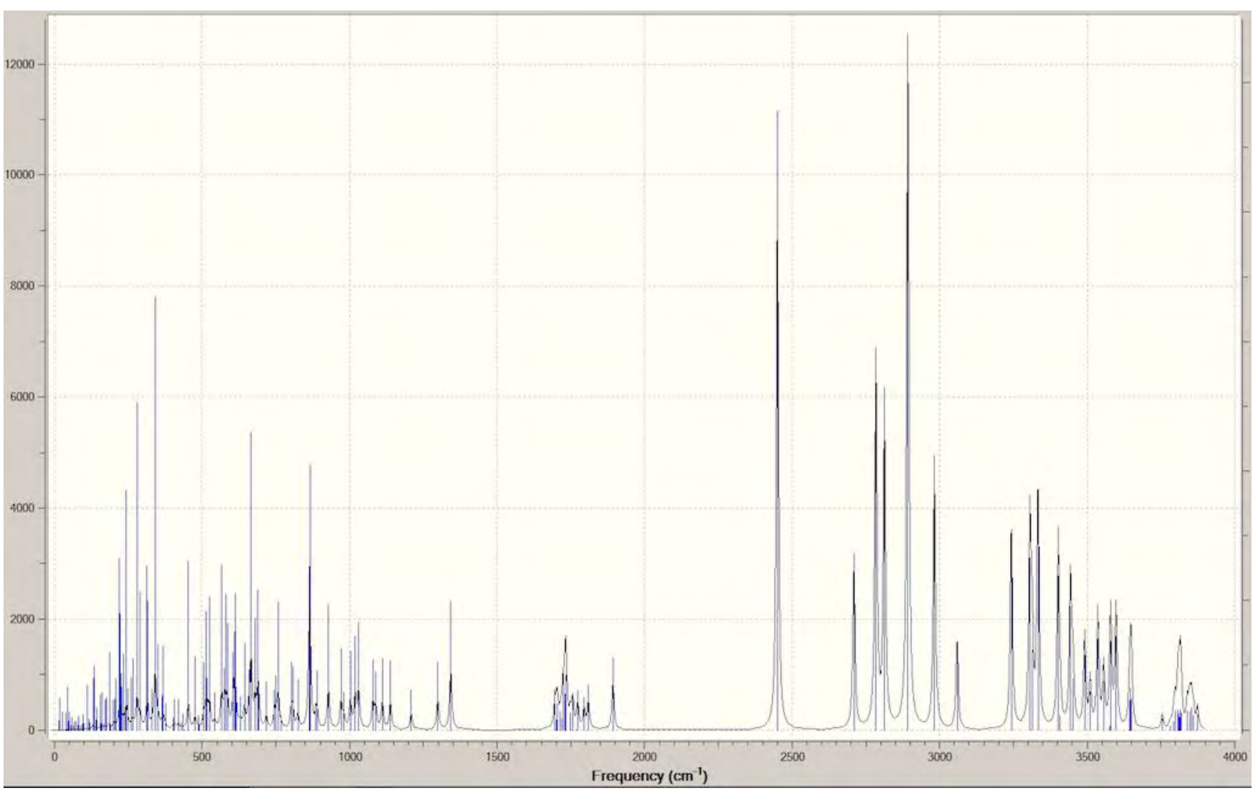

Figure 8h. As^{+3} 20(H_2O)

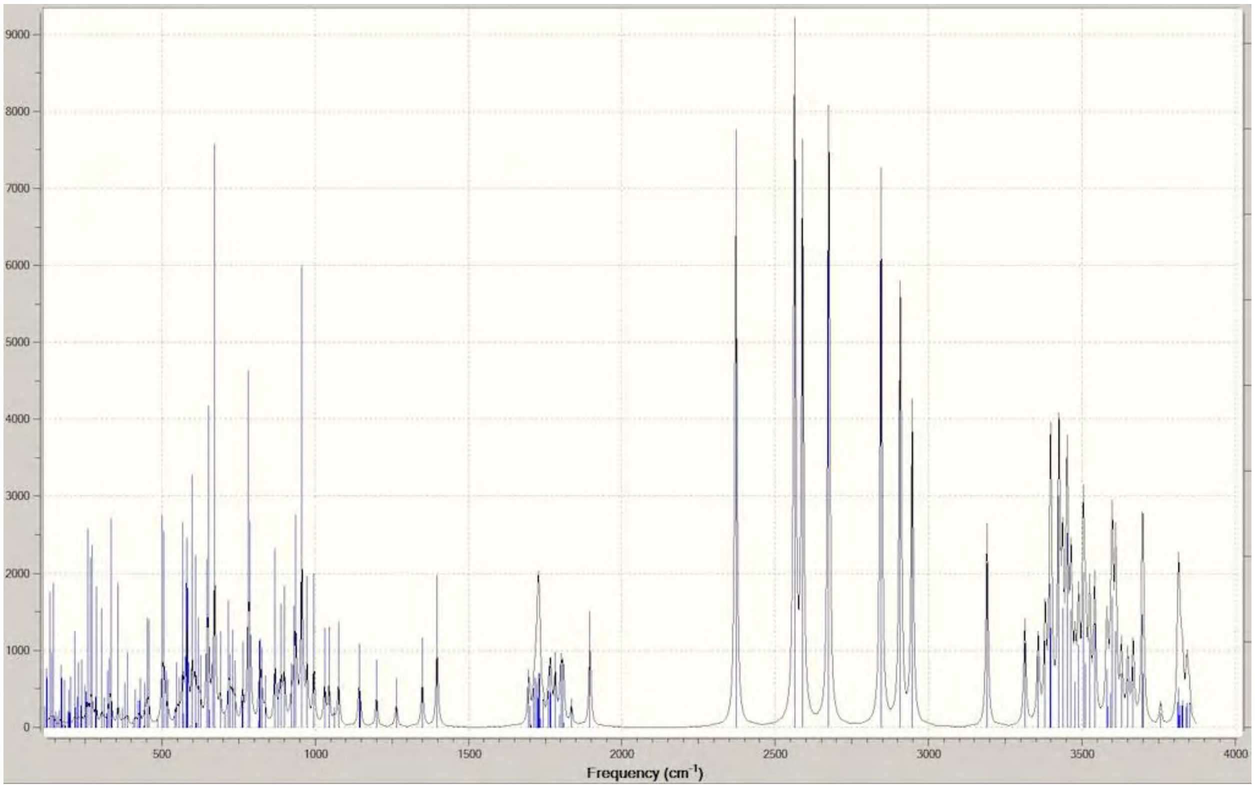

Figure 8i. As^{+3} 24(H_2O)

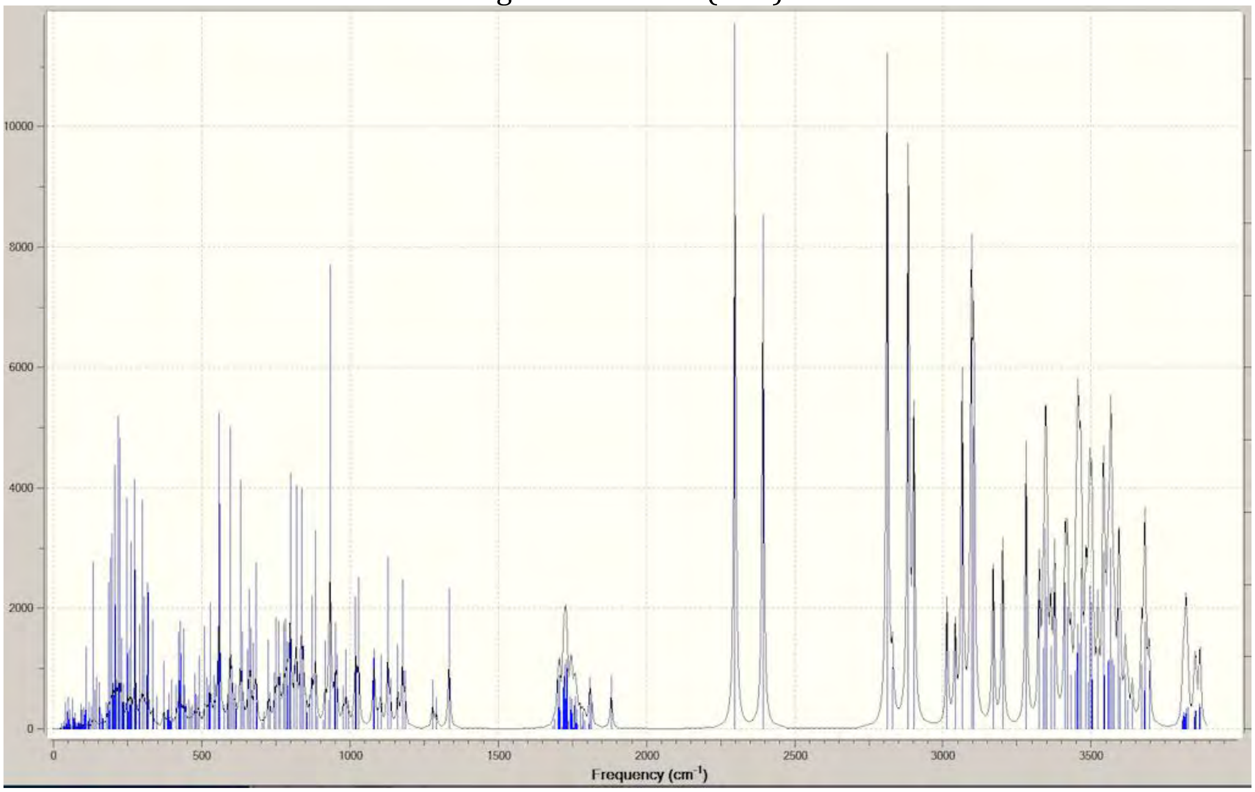

Figure 8j. As^{+3} 36(H_2O)

Figure 8. DFT calculated IR spectra for As-H_2O complexes consisting of 2, 3, 4, 5, 6, 7, 15, 20, 24 and 36 water molecules, without water background. Intensity is in arbitrary units.

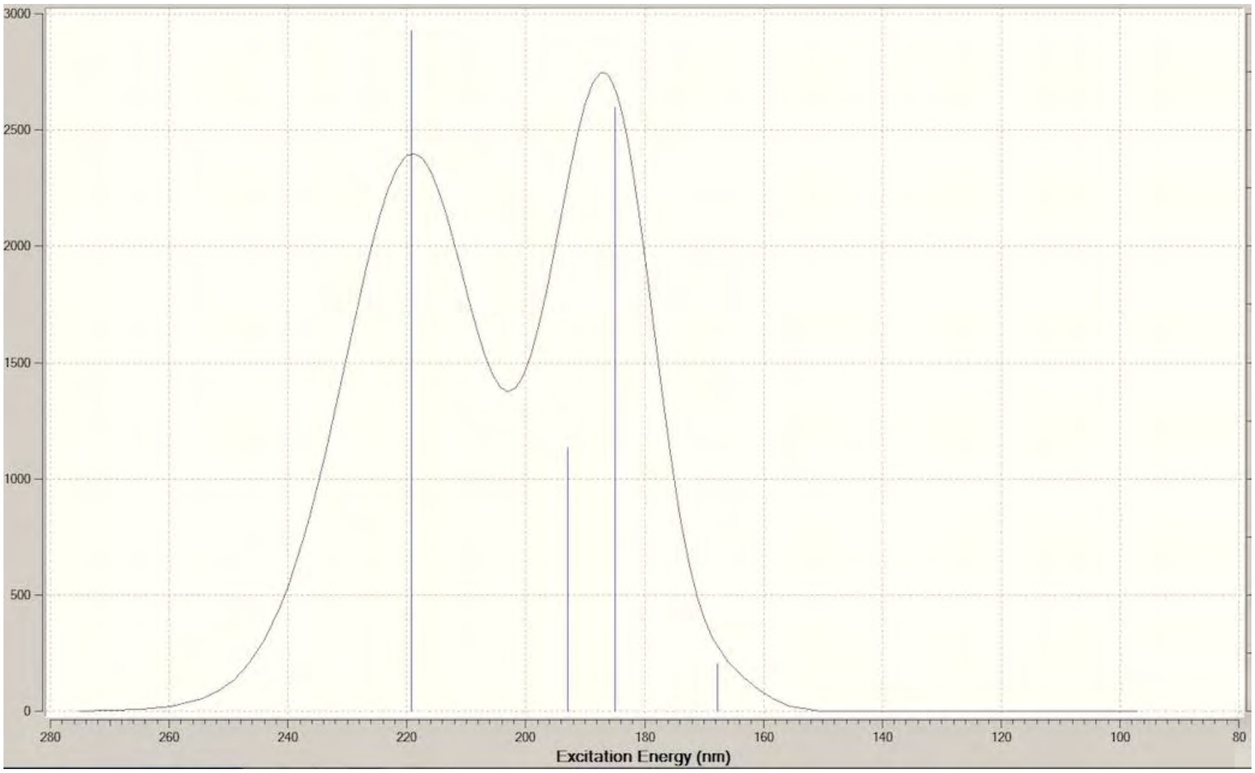

Figure 9a. As^{+3} 2(H_2O)

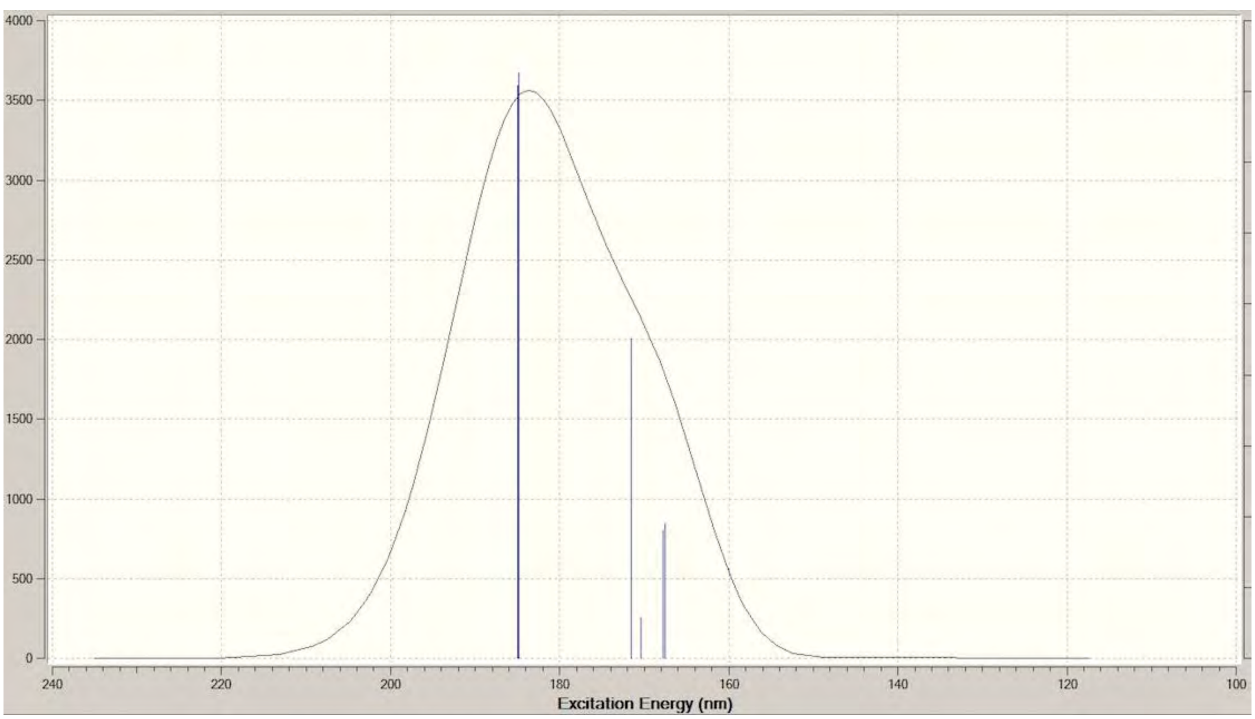

Figure 9b. As^{+3} 3(H_2O)

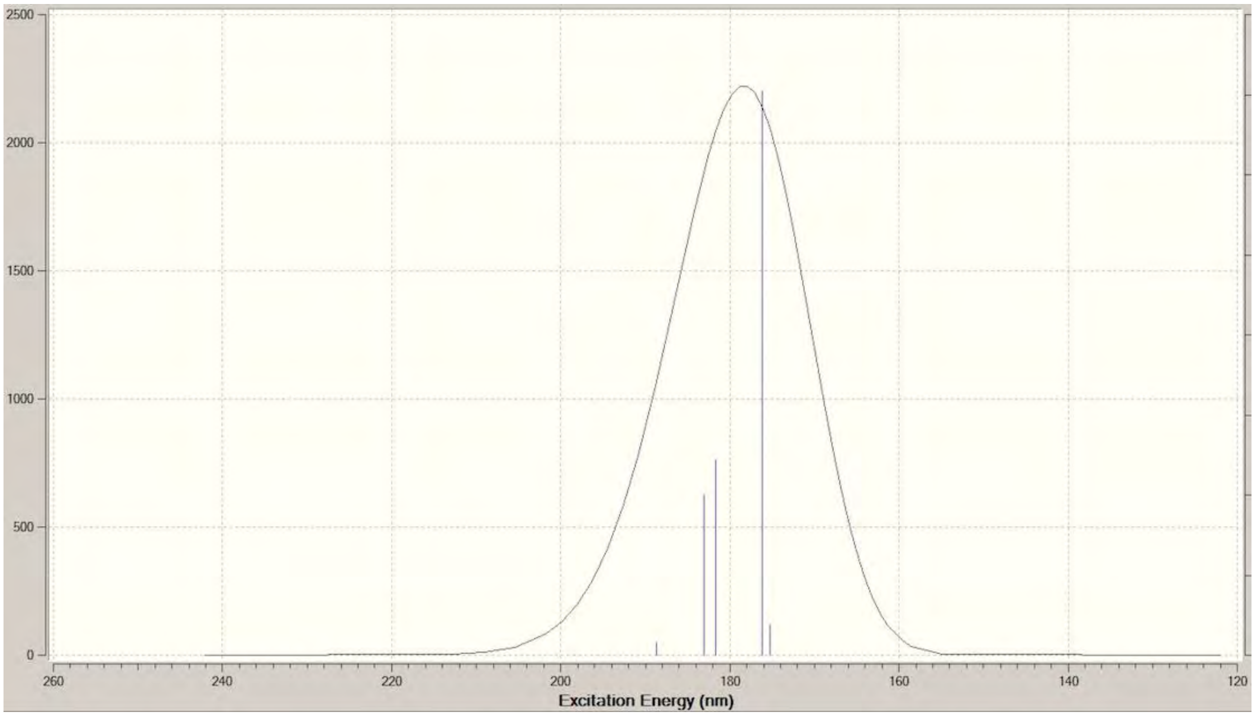

Figure 9c. As^{+3} $4(H_2O)$

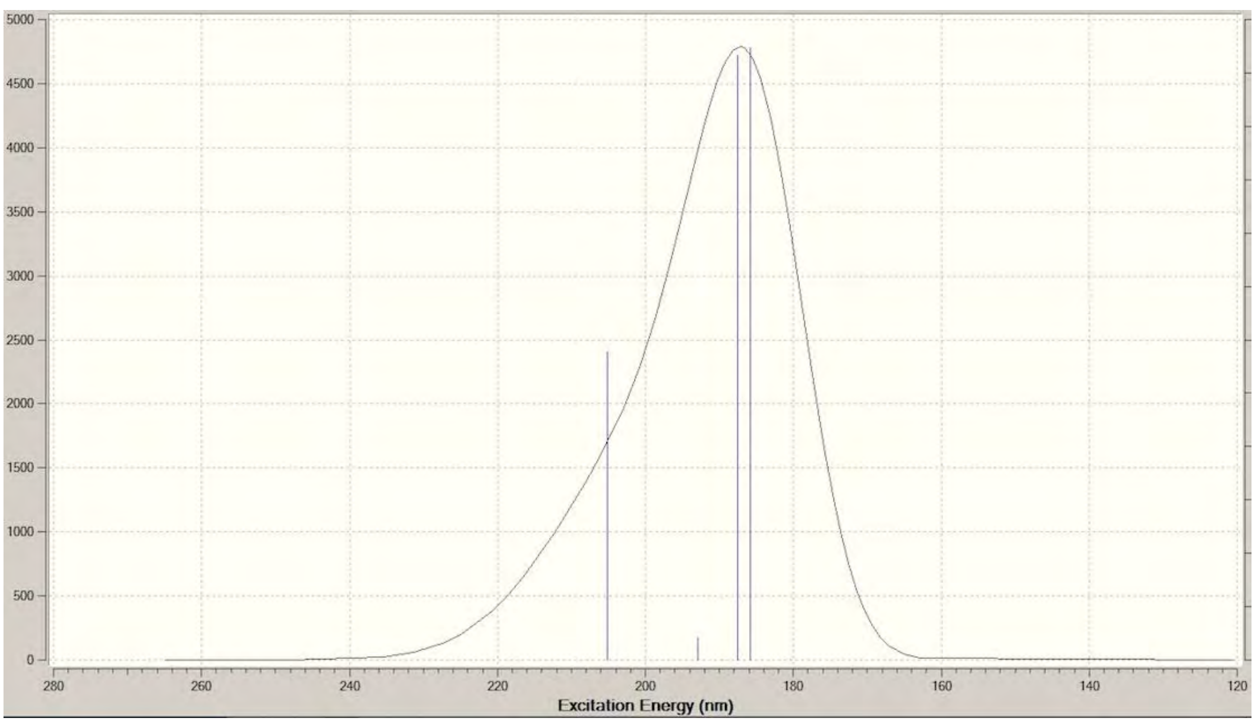

Figure 9d. As^{+3} $5(H_2O)$

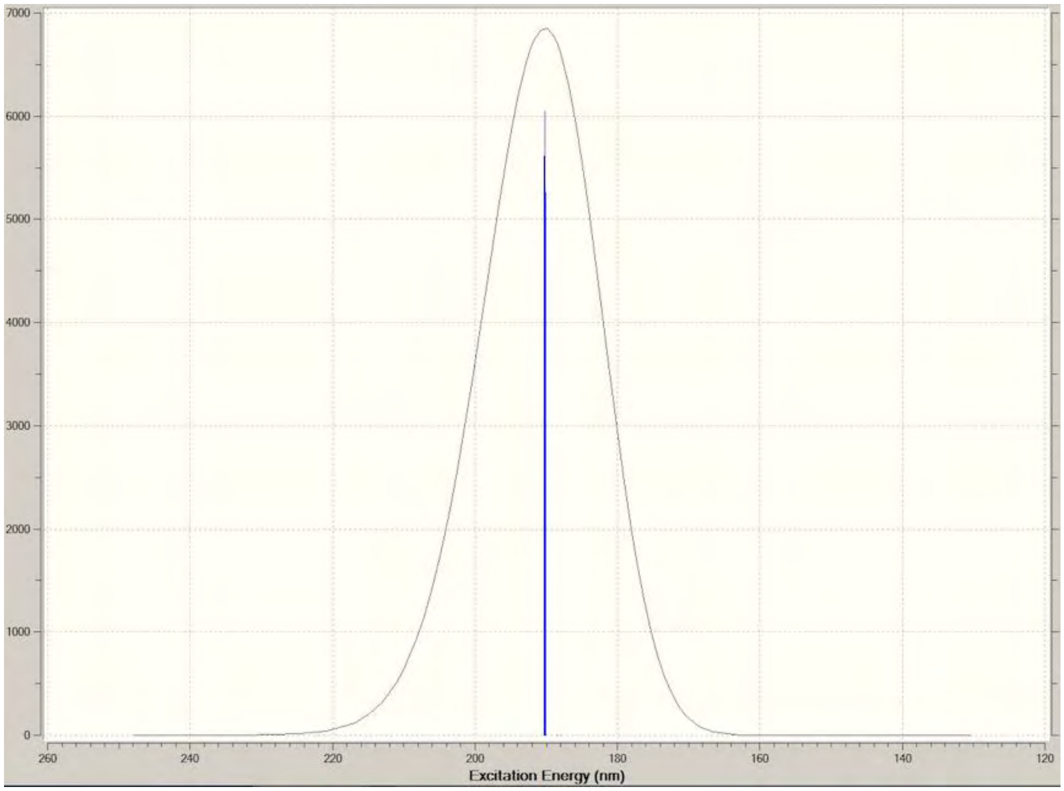

Figure 9e. As^{+3} $6(H_2O)$

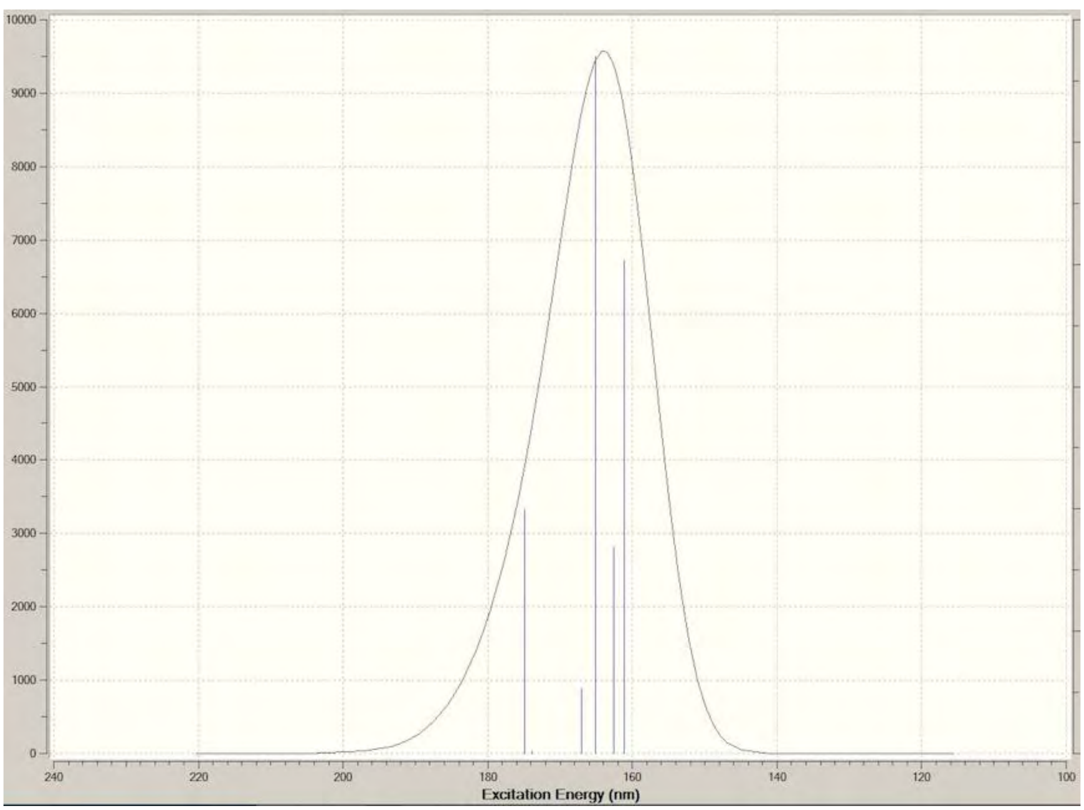

Figure 9f. As^{+3} $7(H_2O)$

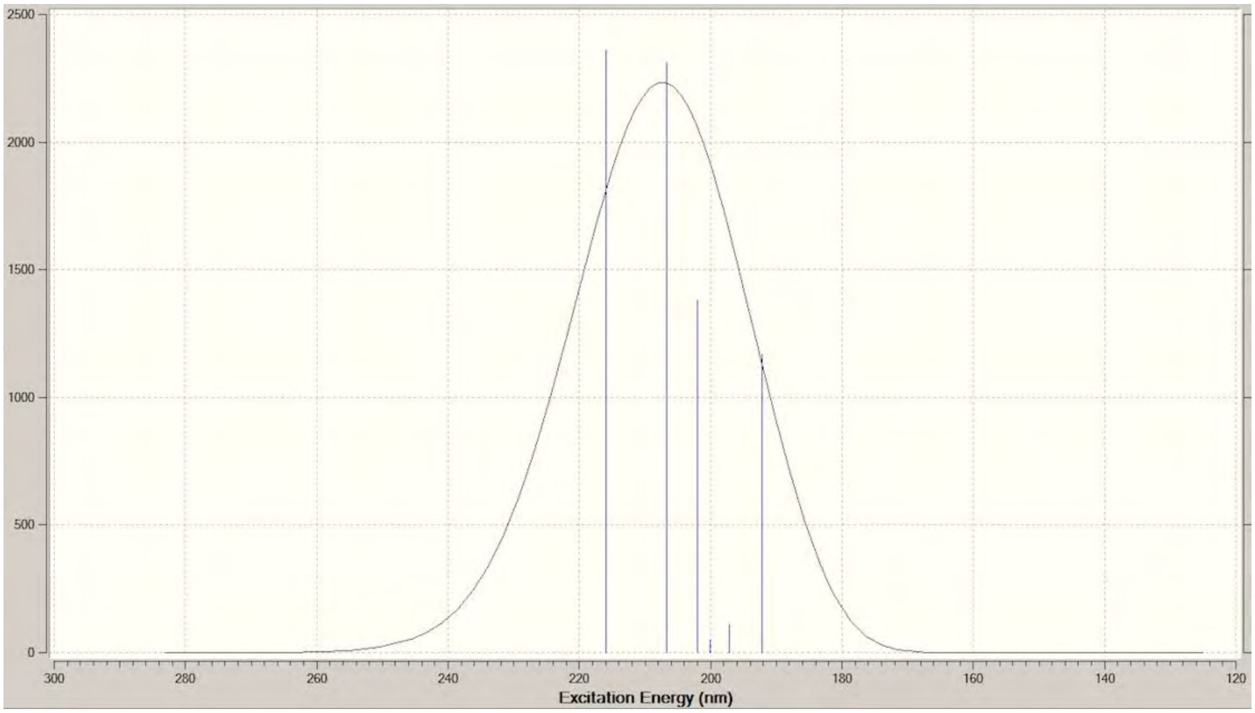

Figure 9g. As^{+3} 15(H_2O)

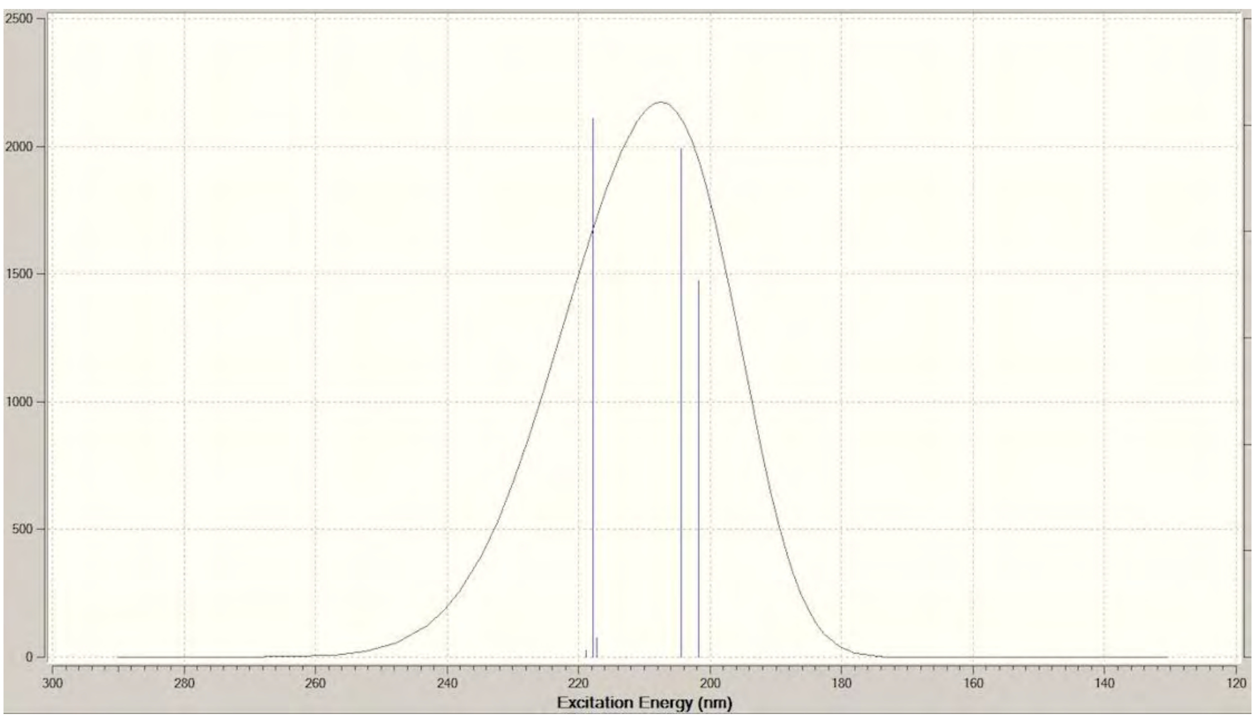

Figure 9h. As^{+3} 20(H_2O)

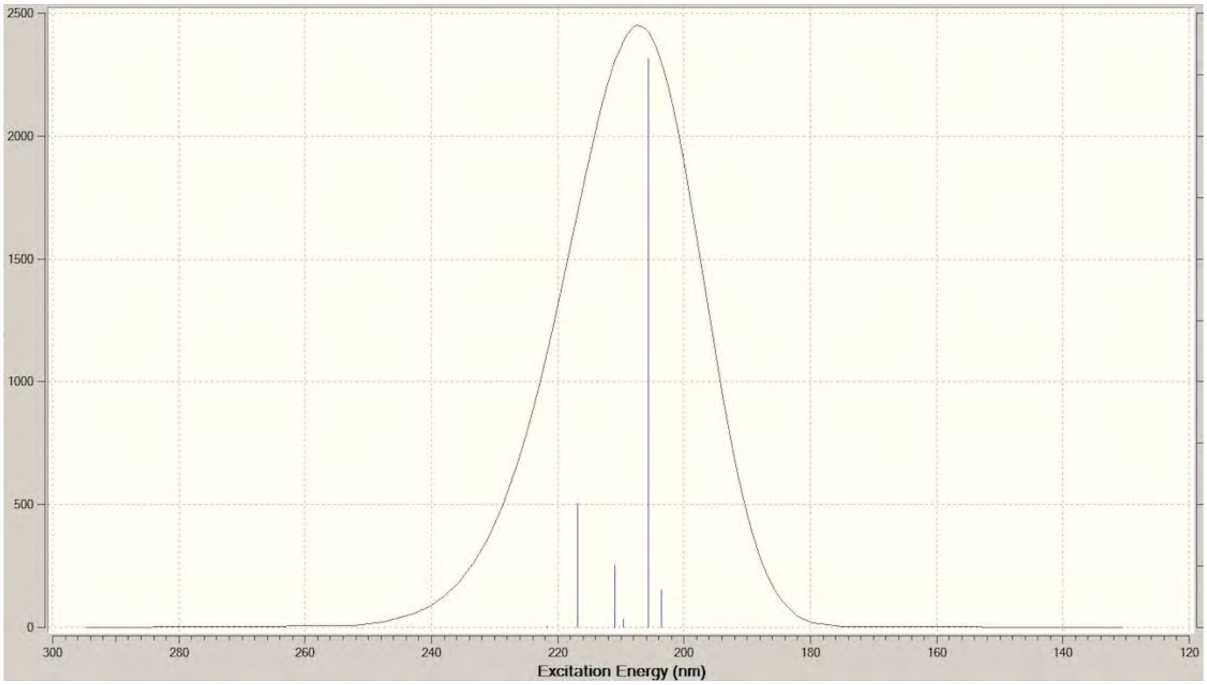

Figure 9i. As^{+3} 24(H_2O)

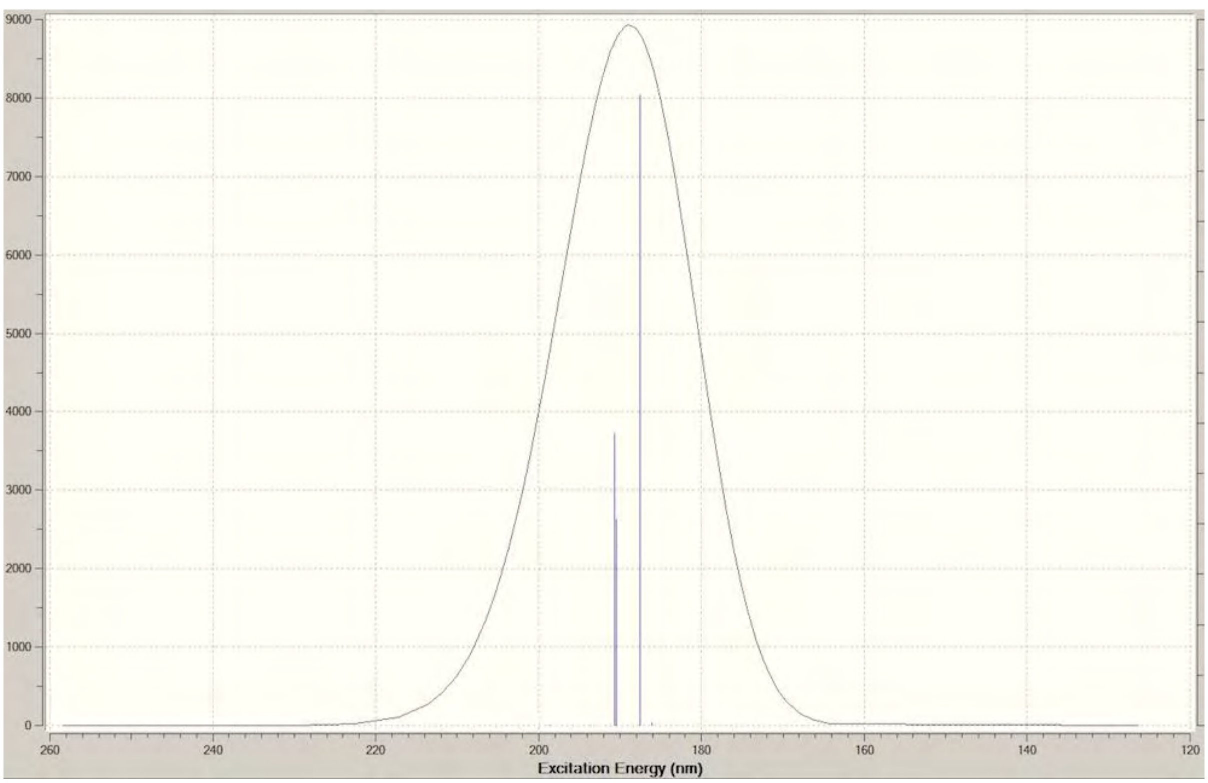

Figure 9j. As^{+3} 36(H_2O)

Figure 9. TD-DFT calculated UV-Visible spectra for As-H_2O complexes consisting of 2, 3, 4, 5, 6, 7, 15, 20, 24 and 36 water molecules, without water background. Intensity is in arbitrary units.

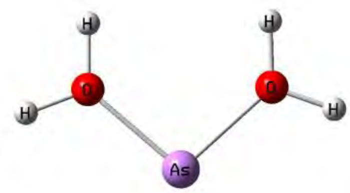

Figure 10a. As^{+3} $2(H_2O)$ in water

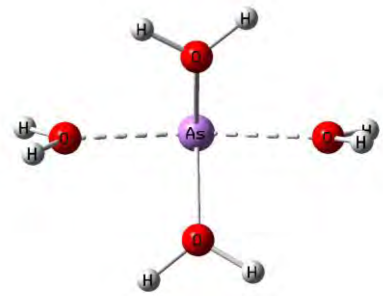

Figure 10b. As^{+3} $4(H_2O)$ in water

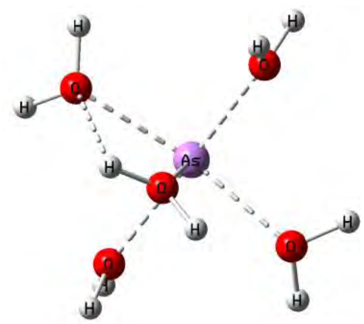

Figure 10c. As^{+3} $5(H_2O)$ in water

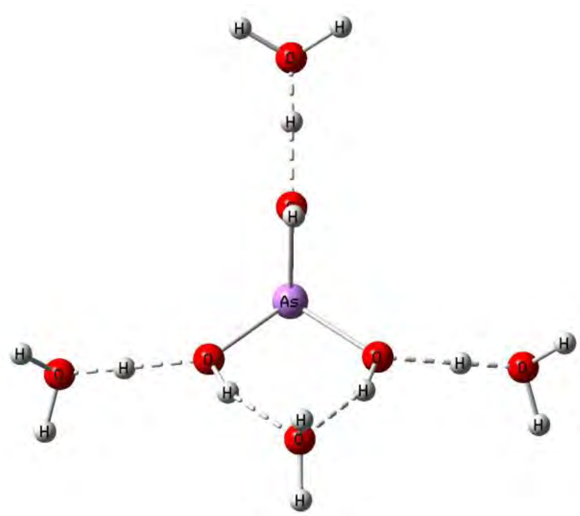

Figure 10d As^{+3} $7(H_2O)$ in water

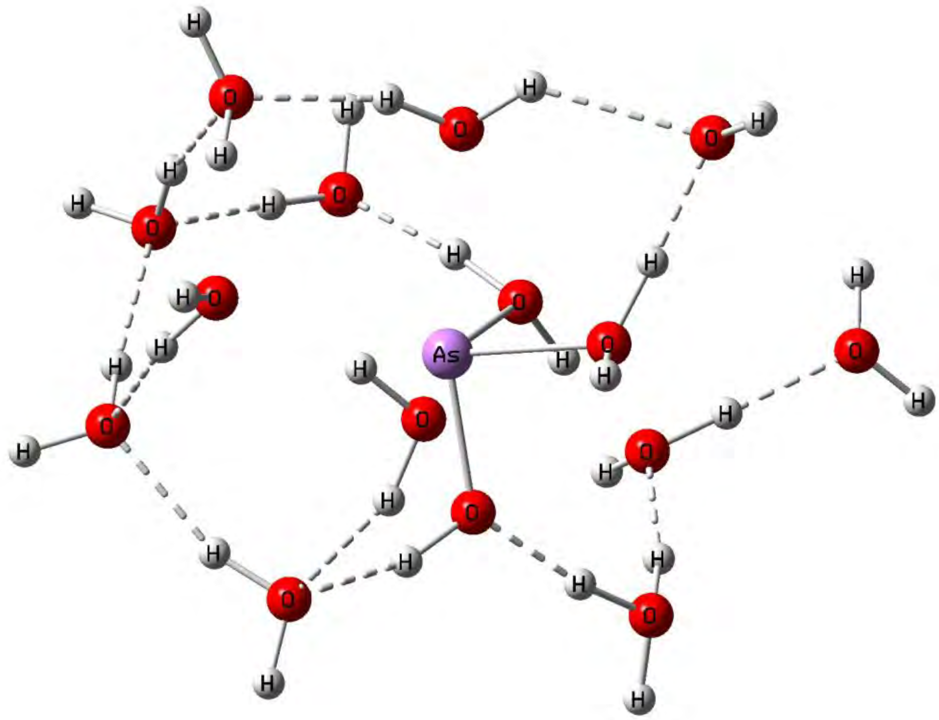

Figure 10e. As^{+3} $15(H_2O)$ in water

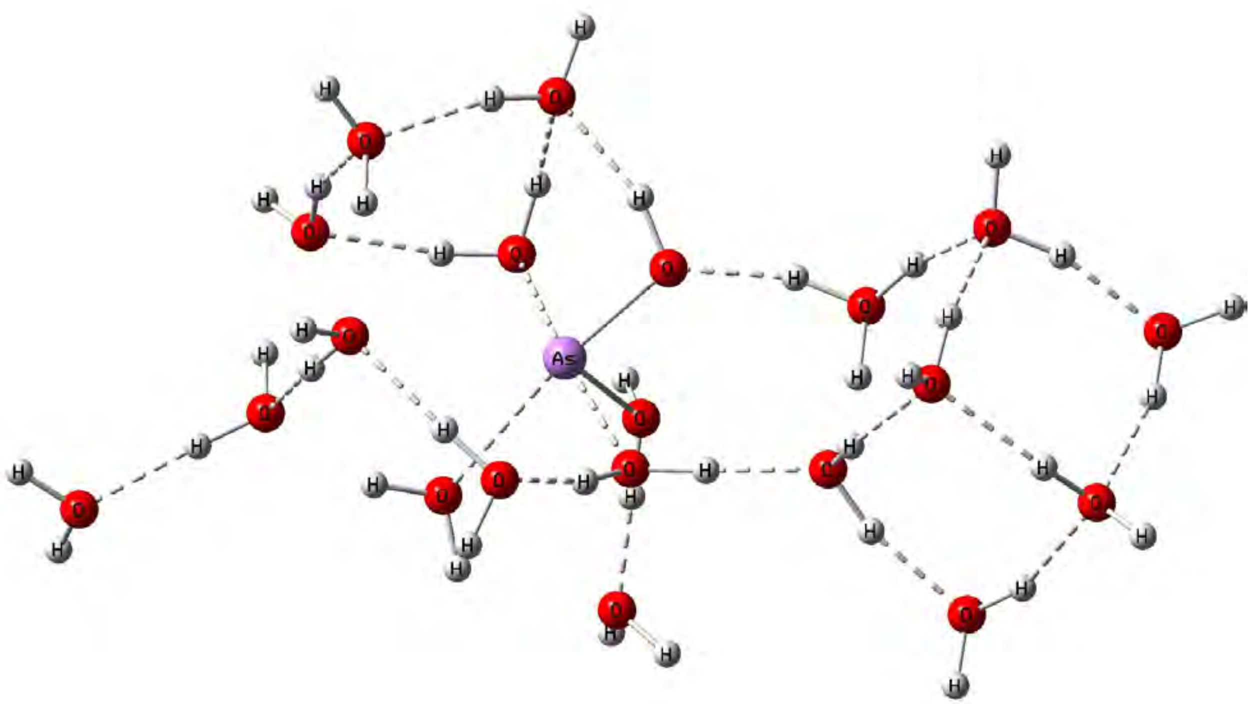

Figure 10f. As^{+3} $20(H_2O)$ in water

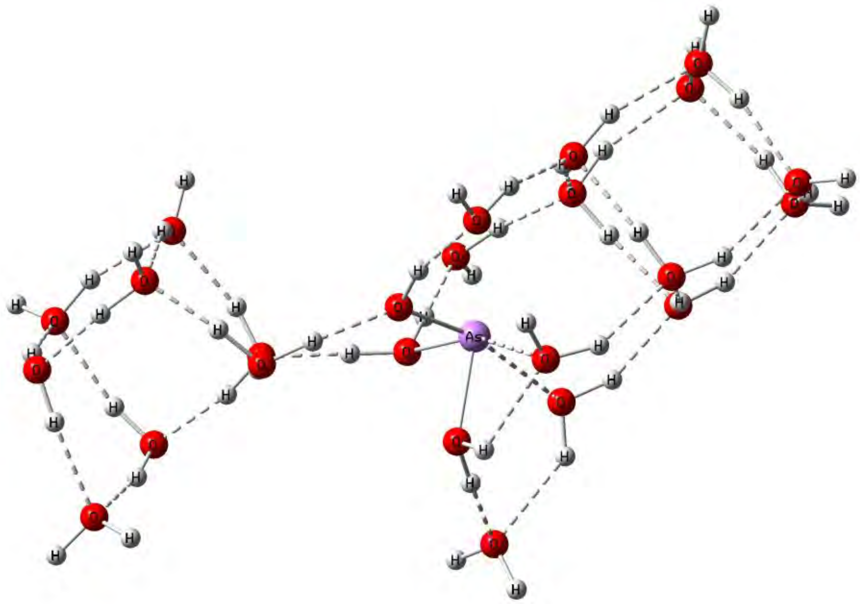

Figure 10g. As^{+3} 24(H_2O) in water

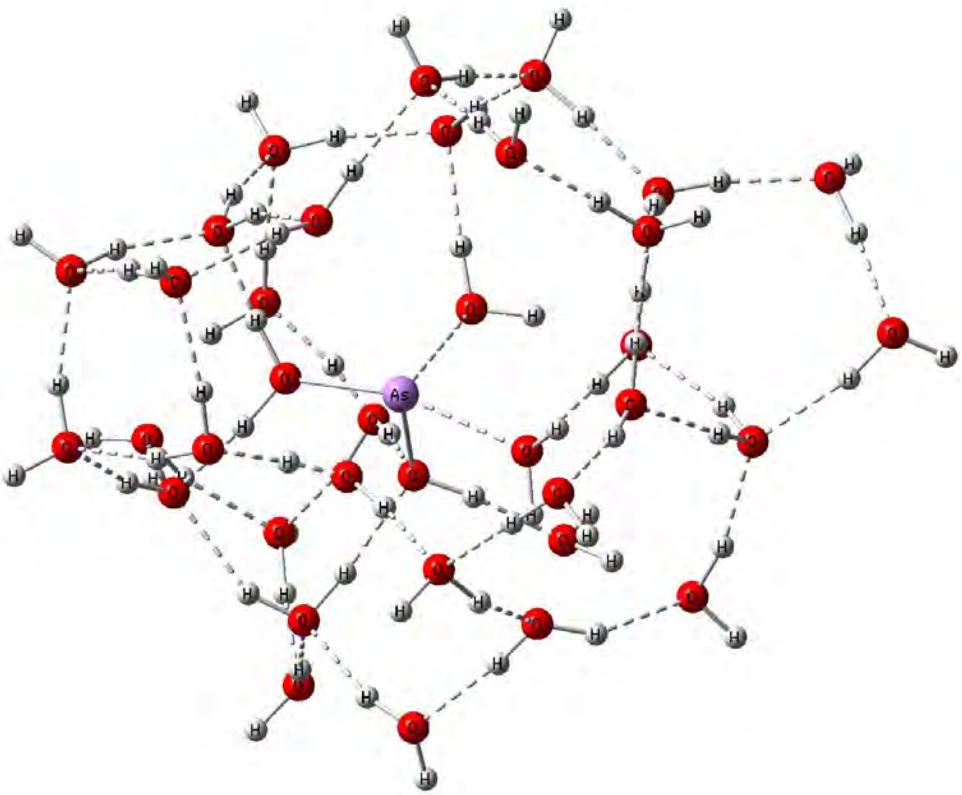

Figure 10h. As^{+3} 36(H_2O) in water

Figure 10. Molecular geometries of As-H_2O complexes consisting of 2, 4, 5, 7, 15, 20, 24 and 36 water molecules, with water background.

Table 2. DFT calculated IR spectra for As-H_2O complexes consisting of 2, 3, 4, 5, 6, 7, 15, 20, 24 and 36 water molecules, with water background.

As^{+3} 2(H_2O) in water

	Freq	Intensity
1	310.3459	1.9609
2	398.8153	91.5356
3	507.2644	1.5124
4	596.5092	142.1594
5	602.5496	26.6922
6	603.6932	980.3323
7	781.0266	2.6026
8	964.9374	54.2390
9	1222.8208	179.0752
10	1731.3759	253.6584
11	1910.8838	77.1332
12	3421.2090	1503.6879
13	3451.6177	145.7432
14	3497.6753	212.0805
15	3509.2209	1214.9919
1	310.3459	1.9609
2	398.8153	91.5356
3	507.2644	1.5124
4	596.5092	142.1594
5	602.5496	26.6922
6	603.6932	980.3323
7	781.0266	2.6026
8	964.9374	54.2390
9	1222.8208	179.0752
10	1731.3759	253.6584
11	1910.8838	77.1332
12	3421.2090	1503.6879
13	3451.6177	145.7432
14	3497.6753	212.0805
15	3509.2209	1214.9919

As^{+3} 4(H_2O) in water

	Freq	Intensity
1	122.4374	75.2791
2	166.4600	5.4119
3	183.9250	0.2910
4	211.6977	1.0529

5	241.4753	8.4426
6	249.1060	25.2430
7	328.8628	4.4847
8	349.4935	142.6424
9	358.0970	247.8650
10	377.0110	0.1078
11	393.2487	103.1777
12	396.8150	0.0070
13	454.3663	471.4978
14	466.8746	187.3336
15	483.3830	421.5410
16	546.2039	210.7991
17	567.2067	372.5377
18	798.2560	15.9820
19	842.7018	157.3815
20	900.0974	0.9866
21	930.0350	163.9780
22	1705.1877	18.0100
23	1708.8710	330.1116
24	1740.6350	236.3790
25	1750.0554	13.8753
26	3612.0601	810.2934
27	3621.7771	90.9180
28	3656.1643	819.8918
29	3662.9500	31.8540
30	3694.9099	25.4630
31	3695.5481	830.2877
32	3743.2683	441.5243
33	3743.4641	337.9660

As^{+3} 5(H_2O) in water

	Freq	Intensity		Freq	Intensity
1	84.7701	5.5345	22	571.0698	57.3837
2	113.4038	93.7666	23	728.9128	6.0889
3	144.2610	2.3450	24	758.8940	141.0960
4	154.1359	4.7866	25	767.4748	16.6130
5	160.8287	3.8287	26	778.4788	143.6055
6	205.4510	3.0440	27	874.0480	103.0800
7	213.9755	1.1243	28	1622.8101	195.4386
8	233.5960	94.9829	29	1707.5718	159.6328
9	247.7790	77.6690	30	1711.2330	78.7840
10	278.4374	109.8983	31	1714.4097	267.4180

11	288.7020	22.4167	32	1716.0684	30.2032
12	303.3710	106.1320	33	3631.0491	356.2760
13	327.6032	8.2020	34	3679.7876	665.0776
14	332.9644	80.4824	35	3682.5742	214.9621
15	355.9150	55.3490	36	3684.9031	423.5640
16	368.0694	862.0919	37	3691.3784	33.4087
17	393.6858	11.8297	38	3729.7915	429.9159
18	417.4260	481.8700	39	3766.2261	336.1250
19	501.1596	5.0318	40	3767.0554	271.9161
20	544.5419	575.3577	41	3780.5127	338.3952
21	550.5520	133.8080	42	3782.4209	309.9760

As^{+3} $7(H_2O)$ in water

	Freq	Intensity		Freq	Intensity
1	13.9486	14.4543	31	654.9240	121.9824
2	31.7094	12.3640	32	745.4506	33.4683
3	43.5420	6.6020	33	818.7830	532.3500
4	61.1078	28.6051	34	1052.6010	66.7840
5	65.1764	36.4690	35	1105.2976	112.2598
6	88.3450	1.4780	36	1185.4330	508.4560
7	112.8655	17.1394	37	1326.1737	258.5215
8	116.7161	98.6621	38	1329.3992	171.4884
9	144.1950	88.6520	39	1400.7340	152.0680
10	151.5111	46.5477	40	1695.1440	1373.2533
11	182.6143	76.7184	41	1703.1754	155.9087
12	185.7550	134.2330	42	1720.6541	117.1510
13	189.9609	10.3340	43	1730.6566	61.4218
14	208.9397	80.4220	44	1732.5573	256.7027
15	239.9920	43.0660	45	1735.9730	158.6550
16	297.6398	467.2412	46	1747.2010	159.1852
17	310.3423	376.9247	47	1923.1865	7162.6670
18	335.4600	9.0930	48	1971.4020	2309.5610
19	372.8043	429.4904	49	2060.0930	2689.9985
20	404.3991	304.6592	50	3265.0520	36.7519
21	462.8440	345.5450	51	3339.5759	2219.2151
22	478.7692	45.6124	52	3712.3711	198.5530
23	490.1961	72.3713	53	3712.6829	134.9723
24	490.7810	219.0630	54	3717.5400	160.7410
25	502.0118	228.6708	55	3766.8406	18.4025
26	512.7051	12.6088	56	3767.6921	198.2226
27	529.5900	201.2540	57	3784.3621	330.7230
28	599.9254	378.2101	58	3784.9521	338.7678

29	614.3513	110.9928	59	3789.9189	332.2890
30	616.6810	265.9930	60	3851.3689	188.3120

As^{+3} 15(H_2O) in water

	Freq	Intensity		Freq	Intensity		Freq	Intensity		Freq	Intensity
1	22.0200	4.0643	34	248.0471	24.2917	67	645.0310	175.7870	100	1753.4755	189.6519
2	28.9715	5.0476	35	264.6880	41.0827	68	678.7600	144.3885	101	1786.5377	111.9980
3	36.7270	2.9560	36	268.7560	26.9360	69	695.0150	47.5600	102	1844.8621	469.0280
4	42.3171	8.1232	37	283.5380	61.4860	70	710.1719	98.9445	103	2520.4668	2220.7634
5	49.5119	11.4296	38	302.1605	336.2341	71	746.2118	446.2172	104	2546.1865	3120.7783
6	49.9610	2.9270	39	311.1800	149.4280	72	779.0400	340.8910	105	2574.6201	3796.6570
7	60.3255	0.1202	40	314.3076	91.3806	73	806.6649	247.2880	106	2759.6387	2173.8181
8	67.2611	6.6618	41	325.2033	135.3859	74	812.3866	131.2118	107	3052.0476	3060.6704
9	73.2940	4.0160	42	343.9520	224.1800	75	845.2850	433.7460	108	3189.1230	1137.9430
10	79.3238	6.8700	43	372.7385	39.6979	76	860.7397	280.5087	109	3217.9912	1137.5955
11	81.2867	12.4495	44	376.3422	66.0209	77	873.3797	136.9377	110	3375.0271	394.6217
12	97.9400	5.2660	45	388.4770	49.0860	78	899.9620	173.5660	111	3382.3960	1100.9430
13	100.7437	2.6673	46	392.4137	32.1519	79	949.1265	256.1313	112	3412.4409	306.9538
14	116.6428	7.4322	47	398.3717	32.6077	80	961.2829	195.3883	113	3436.2002	1170.6689
15	122.6370	33.0930	48	405.5560	216.8350	81	983.8800	79.6890	114	3458.1919	1147.7350
16	127.2148	59.9727	49	410.1776	30.3093	82	1027.5432	201.2490	115	3480.1306	1037.1484
17	129.5719	22.9748	50	425.7847	32.8830	83	1101.5325	196.1046	116	3509.1272	564.3222
18	141.4350	22.9130	51	438.0100	26.6680	84	1105.9790	191.0840	117	3523.2690	218.0470
19	148.4290	18.1410	52	447.5549	35.6507	85	1259.8226	63.7430	118	3582.9153	577.0484
20	155.4750	5.6780	53	476.8390	47.0112	86	1288.4844	542.0081	119	3657.7312	270.3587
21	159.5670	17.1350	54	480.5860	345.6060	87	1326.2830	126.1190	120	3759.1770	374.5920
22	170.4215	62.5612	55	498.0970	28.1959	88	1664.9126	108.8153	121	3768.8201	245.4654
23	177.0466	36.8225	56	506.9851	6.0624	89	1683.5879	223.3683	122	3772.0493	24.0366
24	185.0240	58.1950	57	509.7370	12.1980	90	1704.1610	60.1250	123	3776.4871	31.1070
25	194.5941	18.6264	58	524.4334	300.1017	91	1705.2500	88.7983	124	3804.4280	140.6772
26	198.7263	1.2661	59	537.1786	151.0874	92	1706.2123	188.0747	125	3809.3403	91.9934
27	205.1650	64.3560	60	541.6560	65.1640	93	1712.6260	104.6730	126	3824.8740	120.2050
28	216.3643	18.2283	61	561.1920	94.1743	94	1717.1033	33.1679	127	3832.2852	122.4114
29	224.2701	116.7347	62	563.7473	79.4148	95	1721.4978	332.5624	128	3832.8926	96.6382
30	228.3250	33.5260	63	570.5620	240.2310	96	1726.1420	46.6270	129	3835.4829	127.4970
31	235.2815	66.2917	64	593.8496	289.2263	97	1733.8381	198.6040	130	3840.8999	127.4518
32	239.2221	12.3877	65	610.7896	595.6900	98	1739.7037	16.5310	131	3853.0952	184.8499
33	246.7520	26.9130	66	625.3590	232.5730	99	1747.9740	16.9640	132	3869.6121	136.9530

As^{+3} 20(H_2O) in water

	Freq	Intensity		Freq	Intensity		Freq	Intensity		Freq	Intensity
1	22.7328	2.6820	46	251.1134	9.9921	91	705.0722	70.1862	136	1797.0988	105.4537
2	25.5510	3.7336	47	259.8604	26.7802	92	712.1164	34.3410	137	1898.9581	286.1329
3	25.9850	3.4880	48	262.0060	77.0320	93	713.4750	14.2110	138	2498.8730	3437.7590
4	36.2802	1.1828	49	264.8955	31.5648	94	740.8214	254.6259	139	2625.6506	2886.0586
5	40.1161	0.1737	50	271.5588	91.4238	95	746.0318	306.5470	140	2739.2837	2502.2361
6	46.7680	2.6090	51	274.3440	85.1950	96	770.1940	208.5390	141	2769.6421	1673.4730
7	49.1703	0.9458	52	283.6444	299.0880	97	777.2703	278.6079	142	2921.4514	4450.0942
8	51.5775	10.2533	53	292.5482	35.4071	98	811.5280	325.1259	143	3142.0764	2059.5176
9	53.9480	6.8940	54	300.3080	130.2480	99	821.7630	68.9550	144	3171.5669	549.5380
10	56.6812	2.6929	55	313.3203	96.3856	100	830.2788	542.0980	145	3177.8313	1012.0177
11	62.5899	3.0561	56	321.5598	82.3372	101	843.9240	296.5449	146	3267.0146	616.0350
12	67.8690	4.2600	57	328.7120	58.9430	102	872.3650	50.3380	147	3270.3879	1486.7620
13	70.7902	3.7266	58	330.8237	124.6607	103	889.2860	370.7800	148	3358.7876	693.4015
14	77.9766	4.9362	59	335.5340	177.4297	104	901.2254	258.5483	149	3389.9353	1167.0426
15	79.8880	1.2720	60	346.0010	151.5460	105	902.4310	211.1910	150	3414.1169	1400.5420
16	88.9634	12.7891	61	351.2238	148.3706	106	922.0578	46.5443	151	3416.4241	486.0630
17	90.0696	7.9269	62	364.4971	18.0494	107	974.2376	311.5997	152	3445.8591	1053.0894
18	98.1810	64.2360	63	369.2820	8.8830	108	979.2310	155.9220	153	3455.3220	634.5840
19	102.5353	0.8489	64	375.7131	30.9745	109	988.9820	276.9252	154	3469.9287	926.0406
20	106.2757	2.1363	65	384.5530	16.2436	110	997.9060	37.8252	155	3475.2114	847.4550
21	107.0160	7.3350	66	400.6570	22.0820	111	1033.5990	242.0080	156	3480.8201	186.6400
22	117.2152	11.7845	67	412.4215	80.2524	112	1070.7653	295.6234	157	3504.2812	483.7373
23	120.5784	9.9294	68	415.0391	80.2480	113	1074.2030	171.9815	158	3524.6958	665.1401
24	125.4800	9.9690	69	428.0340	201.4540	114	1120.8660	143.0760	159	3556.7290	397.7440
25	131.6903	1.8995	70	434.0880	22.9804	115	1231.0175	99.0663	160	3558.7151	891.7034
26	146.8893	10.9500	71	448.4134	102.5202	116	1298.0835	200.0848	161	3572.4751	430.4836
27	154.2750	33.9020	72	462.6650	130.1950	117	1369.5010	571.0960	162	3687.2610	256.4170
28	154.8540	5.8503	73	476.7602	108.7314	118	1665.2371	112.2808	163	3768.0095	65.0141
29	168.6358	36.5169	74	499.6907	97.2842	119	1690.2629	228.4111	164	3777.0801	20.6353
30	170.7480	2.9260	75	503.5590	78.3430	120	1694.6030	285.2940	165	3811.4751	108.9860
31	178.7289	103.8509	76	508.5900	65.5337	121	1696.2369	171.7614	166	3813.5603	146.9748
32	185.0917	1.5361	77	514.0555	45.9352	122	1700.8121	68.2060	167	3828.1921	116.2832
33	188.1630	9.3590	78	521.1720	312.4330	123	1702.2350	82.3120	168	3828.5229	92.5410
34	191.8654	6.6944	79	524.1003	364.1025	124	1708.4409	96.2444	169	3831.7249	121.3739
35	199.6023	24.7702	80	530.5449	233.6211	125	1708.6768	10.4480	170	3832.4673	128.0652
36	201.4610	1.8880	81	543.6140	292.6230	126	1714.3770	169.6890	171	3833.3291	92.5100
37	201.9812	75.2716	82	556.3988	128.0710	127	1718.8148	163.4387	172	3834.8982	128.1848
38	212.2144	25.8339	83	581.4472	86.4986	128	1721.2155	181.1402	173	3837.3816	155.4630
39	218.5750	15.7070	84	592.6570	118.5740	129	1725.5940	44.0460	174	3838.9629	55.6400
40	223.5605	9.4839	85	611.2485	233.5904	130	1731.7942	93.6953	175	3841.1028	125.2780

41	224.2640	158.1262	86	623.2261	305.7386	131	1734.9393	144.6243	176	3855.4856	174.2338
42	228.0750	81.0860	87	645.6950	287.5600	132	1738.4530	67.4150	177	3872.0071	114.2270
43	230.9852	29.6096	88	654.0047	176.5800	133	1772.4659	118.3503			
44	236.0122	79.2030	89	674.4788	69.2606	134	1783.5123	188.7255			
45	248.4870	261.0180	90	685.6250	179.4590	135	1784.3940	84.7440			

As^{+3} 24(H_2O) in water

	Freq	Intensity		Freq	Intensity		Freq	Intensity		Freq	Intensity
1	14.2017	1.0317	55	250.5109	48.5828	109	728.6514	80.4712	163	1808.6642	24.1184
2	25.7885	5.1613	56	266.6409	19.2411	110	732.8235	154.9435	164	1812.5919	40.7639
3	32.8380	11.8270	57	269.8000	70.8920	111	744.6970	60.2160	165	1910.2980	391.8570
4	33.8264	2.0396	58	279.0565	79.4456	112	755.4205	449.6340	166	2465.3943	3707.6523
5	37.3090	4.0245	59	282.1558	23.2566	113	758.2993	152.8000	167	2574.8015	2635.3770
6	47.5920	0.5660	60	285.0510	82.5510	114	774.4400	387.3780	168	2634.3540	2730.8350
7	48.9547	1.9346	61	297.3394	87.3241	115	776.4038	639.5012	169	2729.2520	419.4479
8	54.6916	7.4781	62	301.2140	9.9424	116	788.7881	148.2621	170	2790.8013	6425.5913
9	61.0960	8.5210	63	304.4360	35.5680	117	798.7960	235.4890	171	3047.0249	483.3760
10	63.8487	0.9237	64	317.7882	27.7726	118	812.0188	443.0388	172	3054.3872	1496.4989
11	67.1733	3.2119	65	328.3785	73.9508	119	821.0519	80.9355	173	3144.7881	1720.7554
12	70.7710	2.5190	66	329.9260	46.9810	120	830.7750	205.1280	174	3222.1951	1178.9320
13	77.8247	0.7914	67	332.7968	175.1194	121	842.5180	20.9183	175	3306.9453	1425.6382
14	80.7868	0.9650	68	335.9467	109.2766	122	846.2717	438.5351	176	3363.5784	49.1957
15	81.6060	11.1510	69	342.9920	143.0110	123	869.0380	182.8950	177	3390.7581	90.8740
16	89.9484	7.2855	70	344.7633	163.2689	124	871.0725	137.4775	178	3400.3662	662.2757
17	95.8311	3.1576	71	351.8909	50.3819	125	878.8326	77.0342	179	3404.8625	883.6663
18	96.6880	2.6050	72	355.0520	97.7590	126	893.3250	43.2680	180	3417.0811	1048.6040
19	100.1475	8.2974	73	358.7200	65.0597	127	893.8323	1111.6849	181	3438.5605	794.6073
20	105.1829	6.3710	74	368.1919	18.0892	128	923.2586	242.3747	182	3445.5132	1473.3907
21	108.5690	10.0500	75	369.0930	82.6300	129	958.3610	274.6740	183	3450.3250	1038.7810
22	112.6006	8.8137	76	390.7689	10.8107	130	959.6902	171.6398	184	3474.3191	146.3118
23	113.6830	15.0618	77	392.5527	473.6518	131	978.5739	119.2082	185	3488.5176	1326.6505
24	117.4630	23.1690	78	407.3430	163.6590	132	991.3870	197.1820	186	3506.2900	564.0610
25	122.0653	19.6329	79	413.8909	30.4390	133	1028.4279	315.6357	187	3511.3516	969.5684
26	127.2464	17.7262	80	417.6869	31.2012	134	1064.1331	268.0008	188	3523.4490	201.8336
27	134.7890	17.2340	81	445.9280	1.6240	135	1081.4750	210.2900	189	3528.6931	576.5050
28	142.7716	12.4216	82	460.7603	12.4918	136	1103.6284	123.9532	190	3531.3552	732.0505
29	146.3124	13.6687	83	478.6425	140.4450	137	1106.9510	23.0934	191	3549.5459	671.0928
30	149.7700	5.6250	84	480.5110	189.4010	138	1137.2550	149.6130	192	3560.7971	541.6670
31	162.0632	59.2785	85	484.7551	209.8005	139	1288.2681	98.8317	193	3564.7004	307.4019
32	168.4493	26.5274	86	501.6628	42.4068	140	1332.8790	219.5172	194	3575.1558	418.9927
33	173.5060	54.7430	87	517.2720	254.2010	141	1390.1440	601.6420	195	3583.2971	103.0870
34	177.5603	18.7593	88	522.1080	101.1509	142	1659.7784	90.2364	196	3612.4087	1234.2498

35	181.7910	13.6633	89	531.7099	162.5318	143	1691.5300	106.3630	197	3618.0591	519.8895
36	185.5550	2.1130	90	533.2340	175.9400	144	1694.7400	95.3510	198	3626.4231	402.3360
37	187.2521	0.4465	91	536.7693	377.1931	145	1698.9015	178.4692	199	3635.4492	277.9594
38	189.7977	9.7170	92	547.9626	26.0703	146	1700.8860	134.0077	200	3759.9736	361.1179
39	190.3610	46.3540	93	550.9070	146.6840	147	1703.5740	228.0870	201	3767.3740	12.1800
40	201.9696	14.8485	94	555.4923	132.3223	148	1704.0363	137.0469	202	3773.0974	20.4296
41	205.0193	3.0827	95	556.8208	98.1031	149	1705.2087	107.9174	203	3831.8528	47.7574
42	205.6740	13.1020	96	565.6690	12.0530	150	1706.0380	106.7060	204	3832.8701	156.7250
43	207.1327	4.0269	97	579.5822	255.5509	151	1707.5494	90.2159	205	3832.9070	108.7202
44	213.2319	20.1740	98	593.6221	110.0504	152	1710.7617	133.0949	206	3832.9519	78.5190
45	214.9240	3.6520	99	605.0520	196.5780	153	1717.1670	240.1840	207	3835.4309	151.5700
46	215.2815	76.3563	100	615.4357	166.2663	154	1739.9039	66.6831	208	3836.4048	86.6670
47	221.1032	4.9973	101	618.9910	194.7149	155	1741.6335	130.0428	209	3836.4834	129.7846
48	222.1040	21.6040	102	634.7000	154.2750	156	1759.8610	248.3180	210	3839.2930	113.3920
49	229.7555	7.2105	103	636.6378	32.4809	157	1762.8643	228.5722	211	3843.8938	116.9961
50	231.5166	20.1507	104	653.1247	1.9644	158	1777.8760	84.6124	212	3853.6772	181.1506
51	234.9410	21.1410	105	659.0990	191.1480	159	1782.3420	289.4120	213	3856.7461	134.0990
52	236.7385	60.9919	106	664.5444	228.8697	160	1786.5148	46.2561			
53	244.6696	90.2865	107	670.2556	72.5170	161	1790.3120	136.8970			
54	246.3780	47.5570	108	702.9860	152.8650	162	1792.3970	232.3640			

As^{+3} 36(H_2O) in water

	Freq	Intensity		Freq	Intensity		Freq	Intensity		Freq	Intensity
1	19.6771	0.4983	82	249.8072	57.5413	163	738.5682	288.0563	244	1780.6012	74.0556
2	24.6653	1.1490	83	252.2362	34.9802	164	743.7054	131.4774	245	1785.1923	199.4649
3	32.3140	4.0690	84	256.8120	33.9800	165	747.1970	268.3360	246	1787.7371	8.4900
4	33.5021	0.2931	85	260.8237	37.9638	166	750.1766	319.4958	247	1804.4187	284.1520
5	35.5205	9.9648	86	263.9471	104.8378	167	753.0710	2.5886	248	1809.0754	65.7878
6	35.9600	0.8420	87	265.6860	0.8250	168	760.1830	286.6360	249	1868.8030	262.7900
7	37.1850	6.7014	88	268.2126	6.6879	169	772.0935	102.2269	250	2190.7559	1703.3398
8	39.9952	1.4689	89	269.9453	17.4359	170	775.1519	79.1612	251	2198.1501	5594.5605
9	42.8210	2.0260	90	276.7890	11.9770	171	779.3070	129.2660	252	2550.6179	3739.3931
10	43.7571	8.6431	91	281.2799	52.2304	172	784.7900	45.7679	253	2622.4333	3865.9954
11	47.6507	2.5457	92	284.3257	9.6622	173	792.4278	343.7888	254	2890.2974	2253.2266
12	49.7330	1.3500	93	285.1530	4.6260	174	798.8790	223.5130	255	3088.7329	1524.1340
13	51.3522	0.7832	94	293.1621	40.6886	175	805.5234	334.9443	256	3097.5071	1601.8737
14	55.7311	3.7554	95	293.7703	187.1853	176	807.0295	178.1903	257	3125.2781	1511.0625
15	57.3160	2.0110	96	296.5810	23.0740	177	811.5030	256.9570	258	3139.0779	2140.5400
16	59.3651	2.5836	97	299.7974	78.2039	178	815.2810	321.1842	259	3168.3308	1328.5989
17	60.9532	3.2026	98	308.2815	11.7766	179	820.7669	362.9967	260	3191.4878	1650.1298
18	63.6790	4.9150	99	314.0680	89.8180	180	839.5160	79.1940	261	3216.8879	2158.8760
19	67.4258	6.7349	100	322.2948	6.6298	181	842.8664	482.8153	262	3238.7122	2205.2605

20	70.0274	2.3654	101	326.6403	77.4555	182	848.2833	125.7783	263	3305.7400	609.7830
21	70.4980	0.6690	102	333.9100	18.8440	183	855.3410	364.1930	264	3325.5730	1557.1110
22	71.3594	1.6121	103	334.4050	6.5425	184	867.0940	60.9435	265	3327.4888	1357.1412
23	73.7637	6.5138	104	344.7240	50.7782	185	867.2416	137.6433	266	3338.2192	946.5598
24	76.2520	1.0720	105	349.2690	81.9150	186	875.6870	233.1270	267	3359.6331	1384.3459
25	76.6734	2.1729	106	351.7563	208.3189	187	881.4170	216.4619	268	3365.7437	2453.0366
26	79.6861	4.8628	107	354.3149	32.8163	188	883.8429	546.2430	269	3367.6567	285.2131
27	83.4030	12.0120	108	357.3600	14.9770	189	888.3690	290.8760	270	3381.1851	631.2800
28	85.1256	2.1165	109	360.3402	75.1008	190	895.7201	132.3294	271	3383.6934	1731.1801
29	86.6599	12.0269	110	364.6483	79.5861	191	899.7748	95.2430	272	3395.1687	1312.6451
30	89.4390	8.8000	111	378.0840	18.3120	192	911.1850	186.3340	273	3398.2720	275.6400
31	89.9205	29.2270	112	381.5349	27.9260	193	924.0786	298.8657	274	3402.3767	528.6182
32	93.6379	7.4776	113	382.4353	198.5466	194	930.4811	346.8707	275	3408.2307	1275.9774
33	95.3340	2.5100	114	383.3500	79.4610	195	938.1830	190.7920	276	3418.0869	883.1030
34	96.2594	8.7066	115	392.8745	154.2859	196	955.9567	547.1913	277	3423.7273	1224.3218
35	98.9272	57.8352	116	402.9685	221.0038	197	979.1648	47.0410	278	3429.7468	1095.9463
36	101.3050	5.9150	117	405.6220	101.5490	198	985.5610	161.8920	279	3434.0149	511.6060
37	103.5891	7.2290	118	406.0498	39.6168	199	991.7960	207.8667	280	3444.5249	1577.3380
38	106.9636	4.3640	119	406.8970	12.9749	200	1005.7799	431.7258	281	3445.5913	954.5905
39	112.5140	9.0070	120	416.4280	66.8830	201	1015.3240	161.7520	282	3450.6101	393.9460
40	115.5241	3.9340	121	423.7670	27.5216	202	1019.0890	222.7511	283	3455.8164	680.1103
41	119.7845	40.3441	122	436.6857	116.2858	203	1034.7419	81.5295	284	3475.8584	525.6533
42	123.5130	6.6460	123	442.8190	111.9930	204	1048.3560	93.9580	285	3478.7949	645.7120
43	126.6782	20.7357	124	445.0240	75.9348	205	1073.0201	366.0287	286	3483.1321	658.9233
44	133.9063	42.9059	125	455.9884	113.5682	206	1098.0201	125.9086	287	3493.6865	851.5375
45	136.8700	8.3380	126	458.0150	7.0030	207	1103.2170	122.2540	288	3496.9409	274.5840
46	138.8536	51.7778	127	460.9875	53.1592	208	1125.7050	211.5610	289	3501.5486	795.4073
47	141.9715	19.1888	128	487.6720	39.1449	209	1221.1475	371.3326	290	3502.0012	674.3003
48	145.6120	23.8080	129	496.3430	139.2590	210	1243.9919	46.2620	291	3505.4861	365.4470
49	149.7099	11.8454	130	500.4046	126.1911	211	1256.8208	133.4543	292	3512.8816	819.1910
50	153.1463	15.2930	131	505.4809	8.3420	212	1259.2700	156.6753	293	3515.1389	260.0555
51	154.5250	16.6590	132	512.9460	228.2730	213	1336.6840	573.6630	294	3526.6870	518.5590
52	163.0167	17.5664	133	515.5483	143.1296	214	1685.7751	146.3154	295	3539.7996	519.0452
53	166.1299	2.4863	134	518.1869	9.8126	215	1687.2028	215.9318	296	3576.8418	613.4624
54	172.4760	44.2960	135	518.4420	92.8600	216	1688.7800	139.0900	297	3580.8989	501.4390
55	173.9456	49.7127	136	519.8781	222.5267	217	1693.6707	170.1232	298	3583.0857	339.1714
56	176.2715	49.4221	137	534.7547	39.8737	218	1695.4563	162.2764	299	3588.2439	711.1633
57	179.6350	1.9550	138	537.4020	97.1810	219	1696.3530	20.2310	300	3618.5071	568.4570
58	184.8368	2.3108	139	545.9178	95.8243	220	1700.4124	62.9484	301	3619.6360	776.4284
59	192.3834	10.1405	140	550.2866	132.2253	221	1700.7264	152.1289	302	3622.3313	304.6964
60	192.6560	89.2870	141	556.3750	263.1200	222	1703.2130	36.3760	303	3815.9929	113.7100
61	193.9300	29.8672	142	561.9106	55.4014	223	1703.6350	93.1516	304	3818.8923	72.6558

62	200.2650	26.8740	143	577.9042	91.7492	224	1705.1198	160.3651	305	3823.2727	98.7666
63	202.7130	42.3750	144	582.3040	142.2800	225	1706.6520	419.8960	306	3824.3210	104.6190
64	203.1749	91.8083	145	589.1821	203.4645	226	1712.8879	284.3308	307	3829.0957	78.8956
65	209.6890	33.1711	146	592.4445	183.8008	227	1716.0793	153.2960	308	3829.8862	92.7341
66	210.1890	36.8300	147	596.7210	104.5930	228	1719.3199	27.2200	309	3831.2280	114.7560
67	213.6759	188.6340	148	600.8943	37.8909	229	1723.9749	176.4478	310	3831.9355	111.6329
68	215.2144	201.7354	149	606.1501	290.4632	230	1727.0153	36.9269	311	3833.1169	76.2373
69	217.1210	196.6610	150	623.4690	190.2930	231	1728.3770	14.4850	312	3834.6130	129.5720
70	219.6852	20.3074	151	632.5252	165.5971	232	1730.7069	329.8794	313	3834.8501	93.9378
71	222.0340	116.8436	152	642.8821	81.7621	233	1731.9603	48.3422	314	3837.2874	70.5201
72	227.4790	7.1190	153	648.8770	59.3930	234	1735.3900	36.9980	315	3837.4319	103.6670
73	228.7731	59.7436	154	672.4621	134.7640	235	1736.5642	134.7800	316	3837.5420	71.8599
74	229.6847	25.3307	155	677.4510	74.3862	236	1737.2271	60.3113	317	3837.7876	112.3957
75	231.2720	109.9530	156	684.8550	292.5950	237	1739.9500	96.1080	318	3838.7229	115.5890
76	233.8869	154.9098	157	694.2168	196.5218	238	1747.5048	85.2535	319	3838.7273	35.9418
77	235.4701	24.1405	158	695.3825	14.2610	239	1749.3822	48.3816	320	3838.8960	142.2052
78	238.0270	37.2880	159	699.8950	325.5430	240	1751.0320	64.9550	321	3839.0049	117.9820
79	242.3257	57.6194	160	708.7212	151.0419	241	1762.4445	63.1930			
80	244.6200	280.6857	161	722.3592	43.8998	242	1770.3820	54.8936			
81	247.0740	29.7750	162	732.8540	183.2150	243	1776.5750	162.1620			

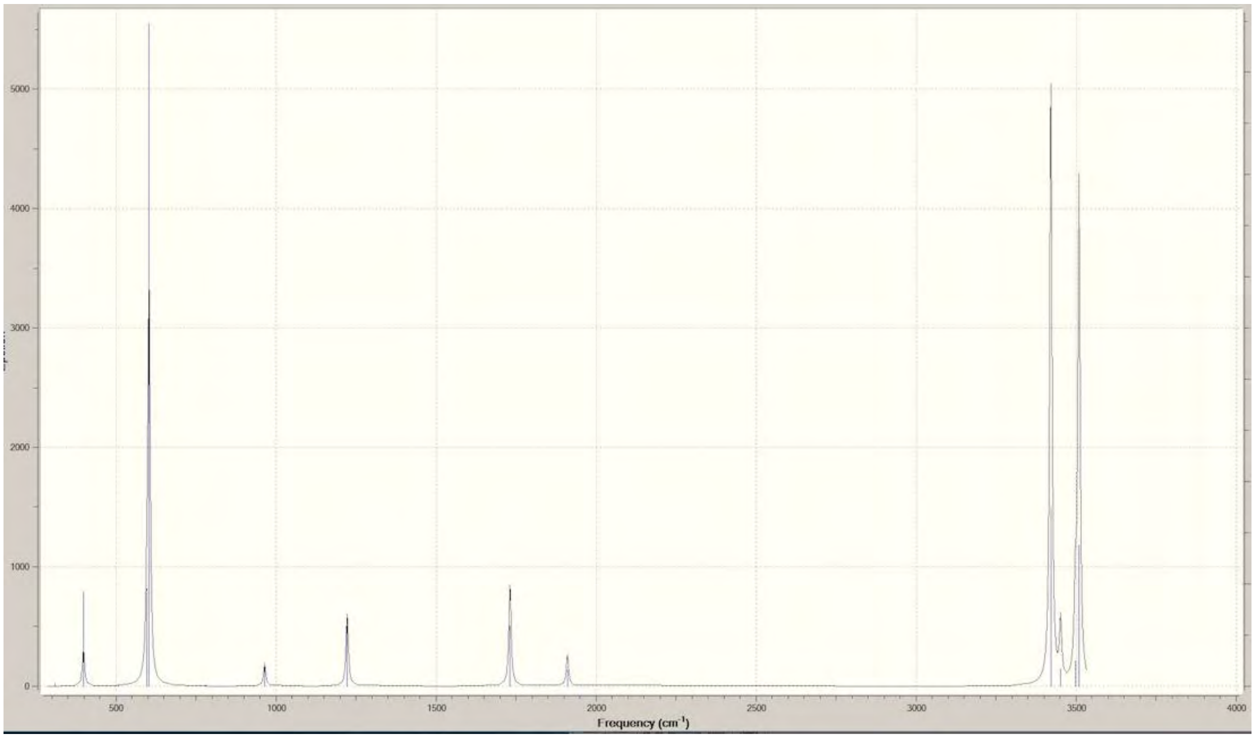

Figure 11a. As^{+3} $2(H_2O)$ in water

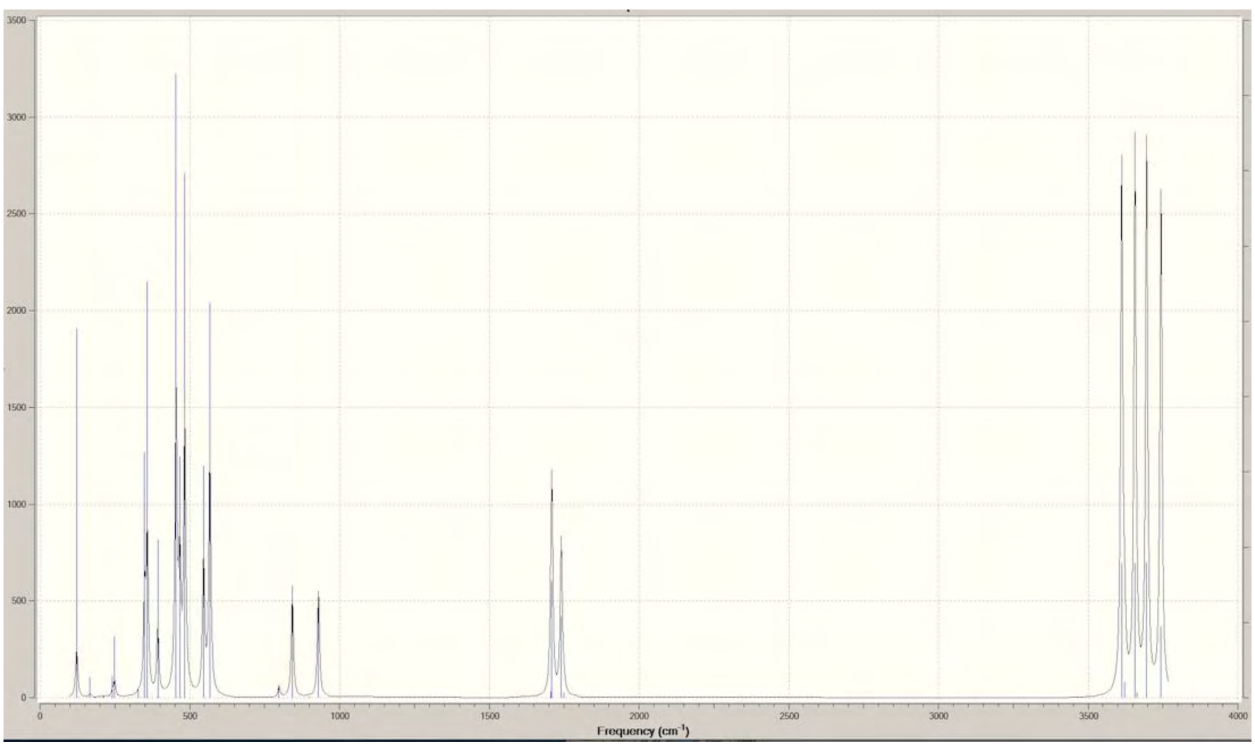

Figure 11b. As^{+3} $4(H_2O)$ in water

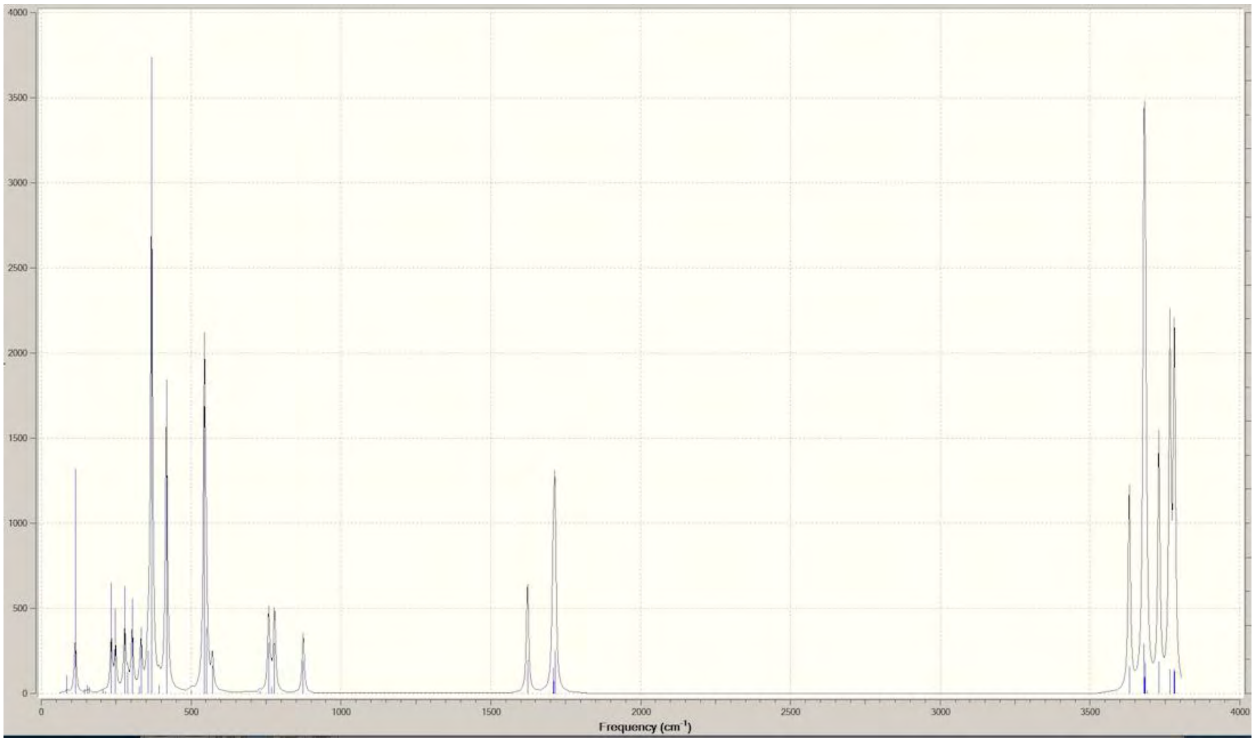

Figure 11c. As^{+3} 5(H_2O) in water

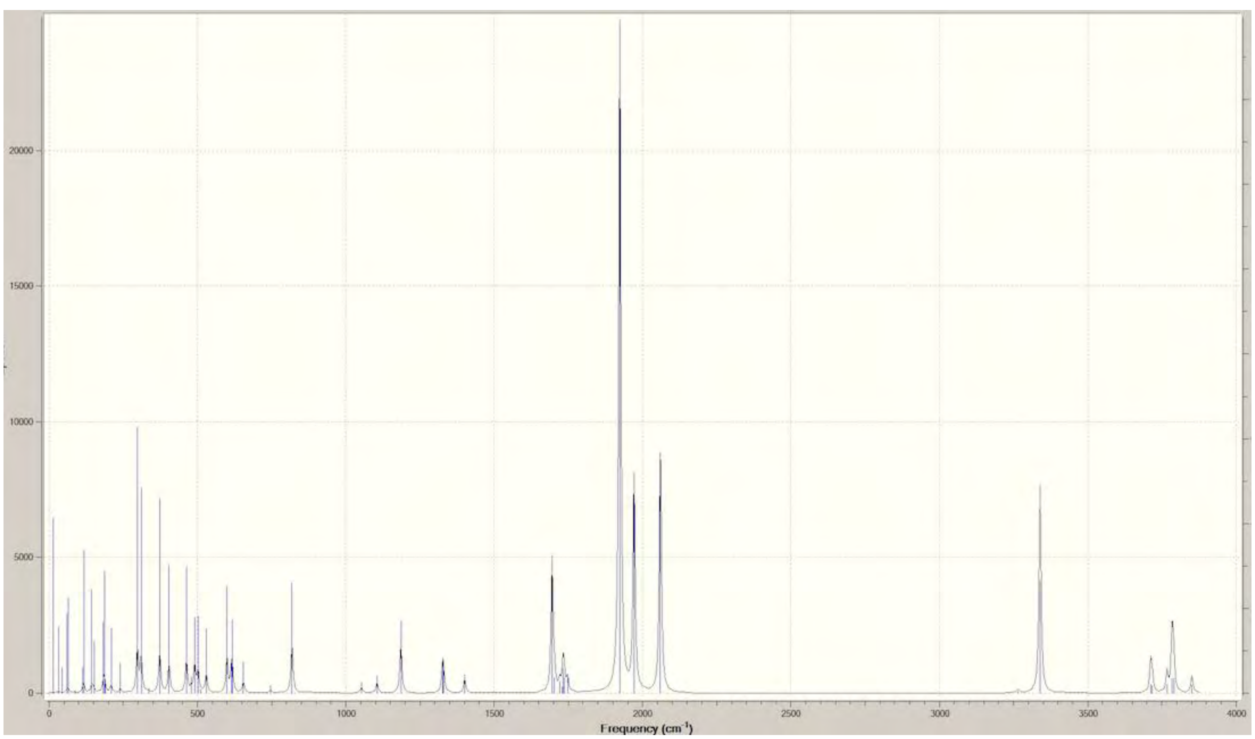

Figure 11d. As^{+3} 7(H_2O) in water

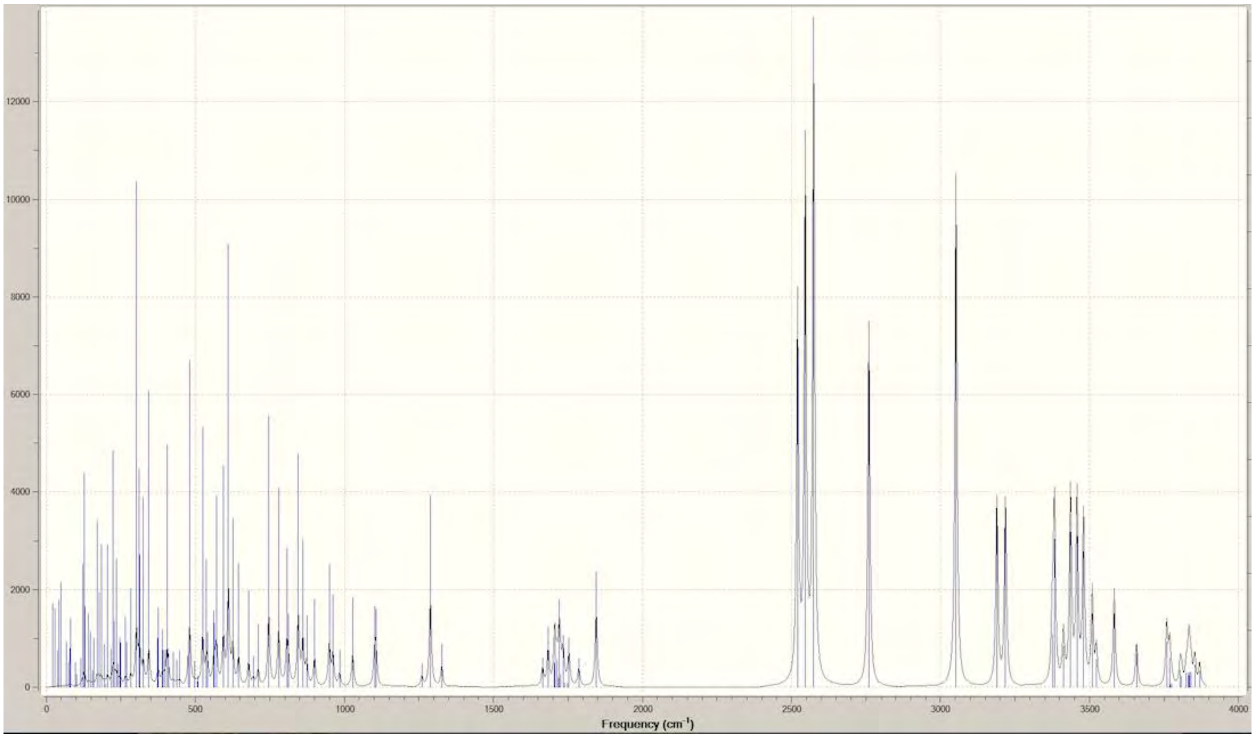

Figure 11e. As^{+3} 15(H_2O) in water

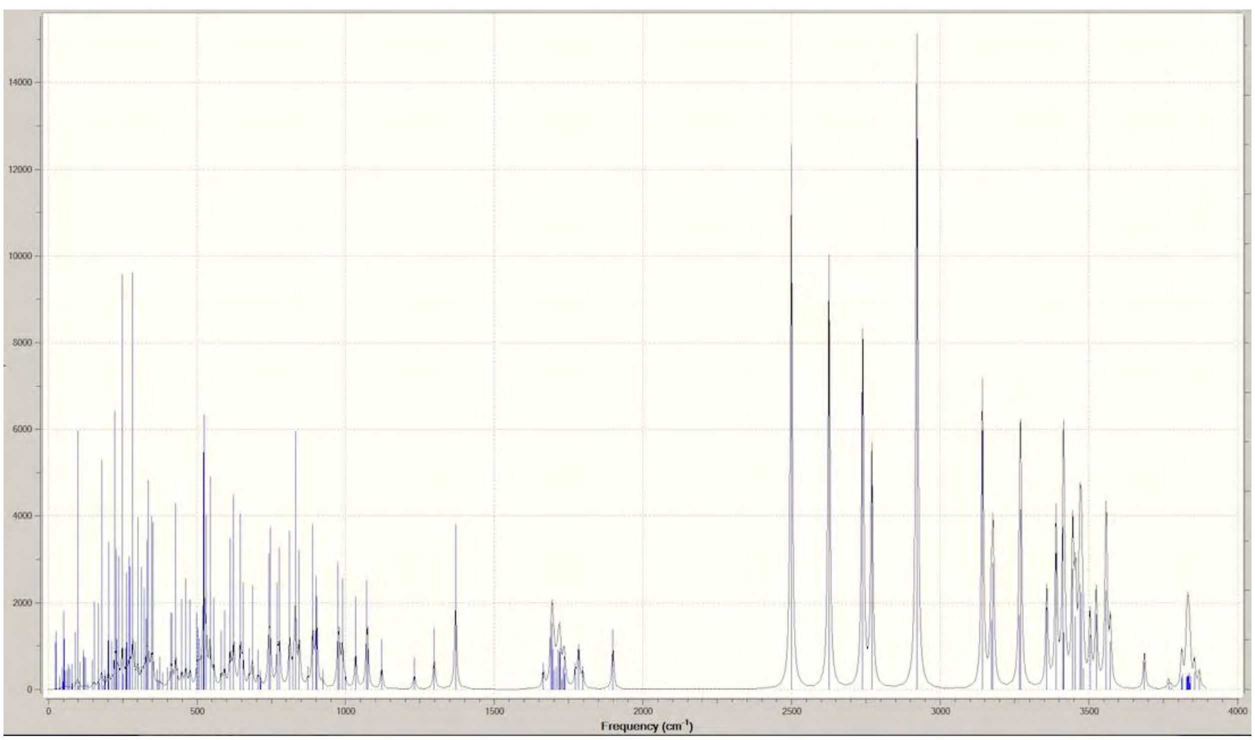

Figure 11f. As^{+3} 20(H_2O) in water

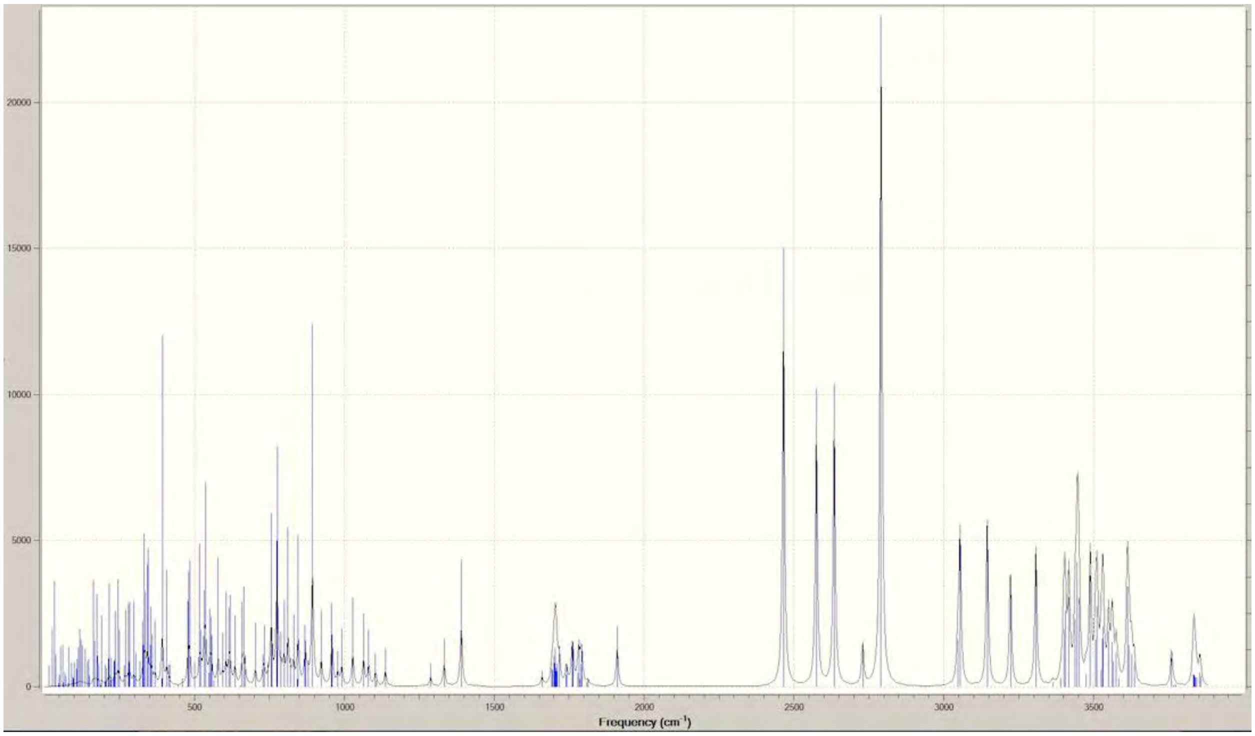

Figure 11g. As^{+3} 24(H_2O) in water

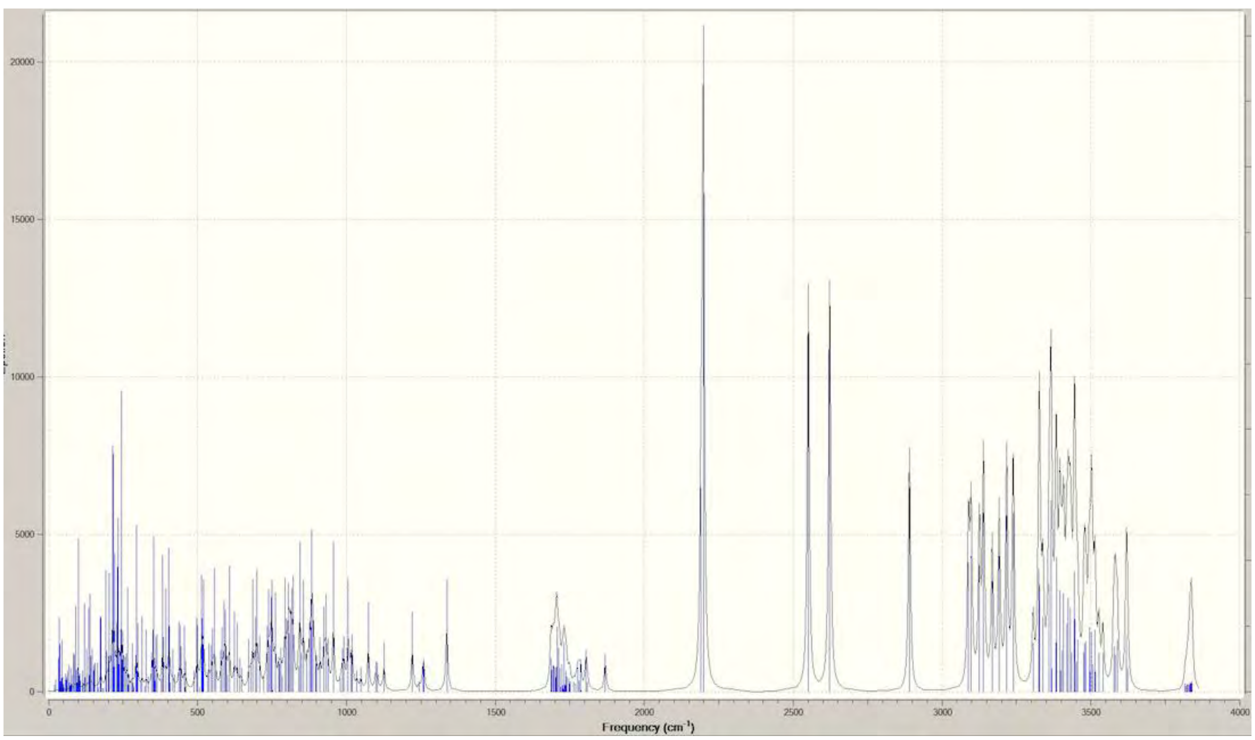

Figure 11h. As^{+3} 36(H_2O) in water

Figure 11. DFT calculated IR spectra for As-H_2O complexes consisting of 2, 4, 5, 7, 15, 20, 24 and 36 water molecules, with water background. Intensity is in arbitrary units.

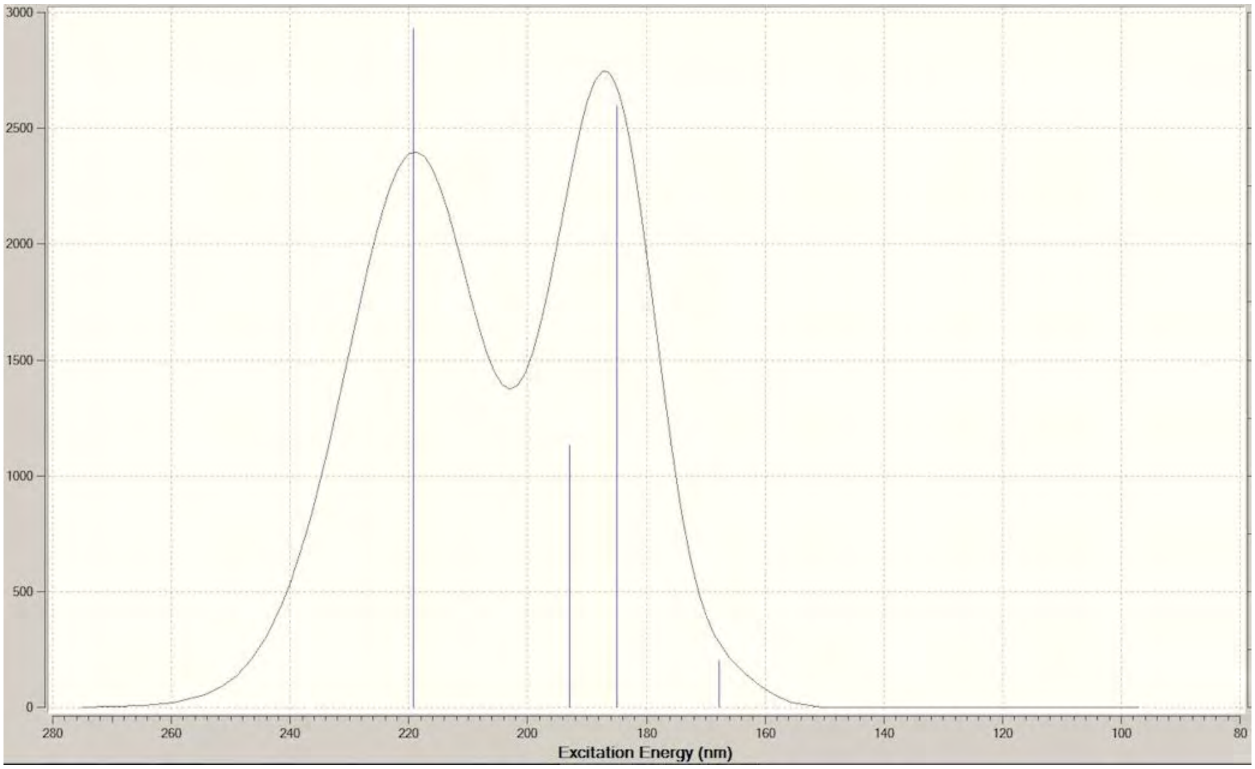

Figure 12a. As^{+3} 2(H_2O) in water

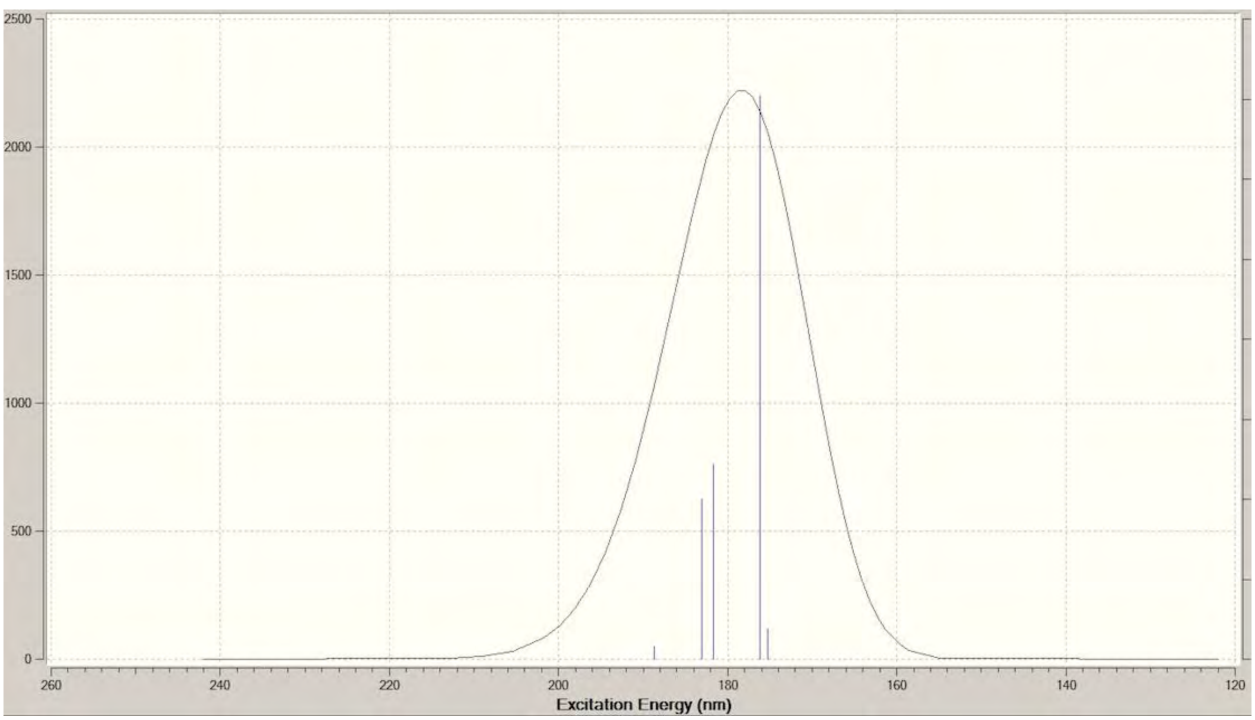

Figure 12b. As^{+3} 4(H_2O) in water

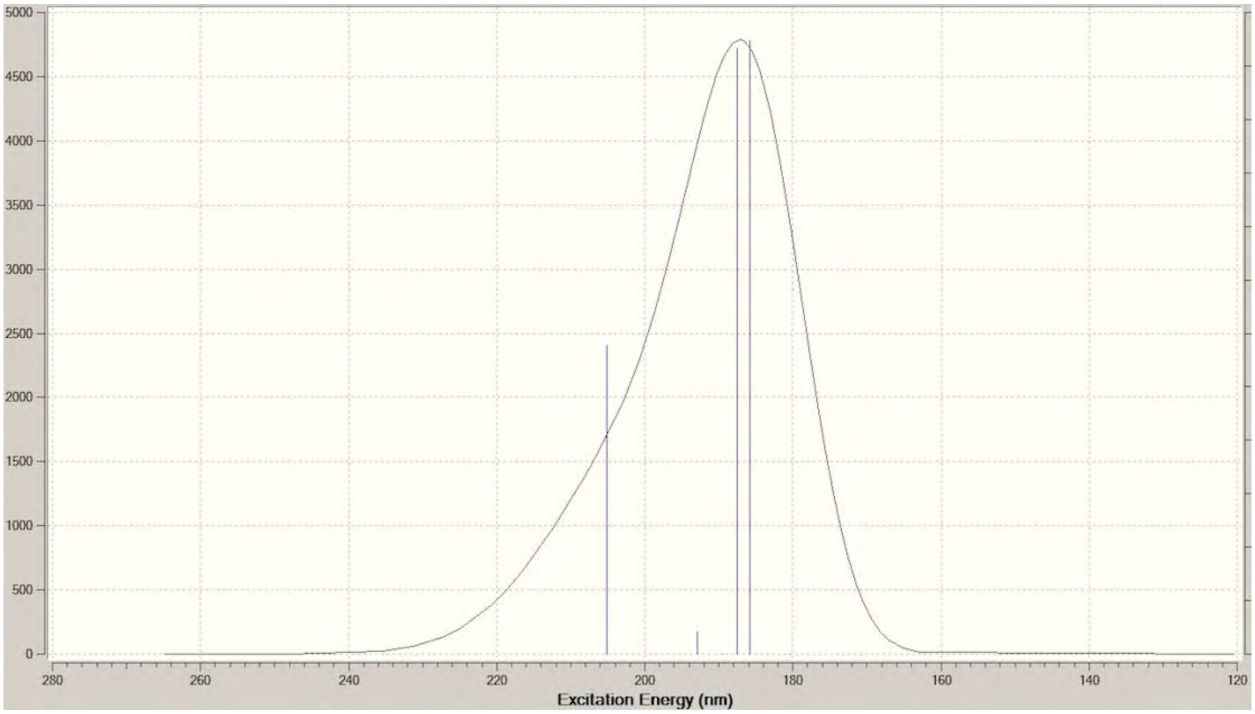

Figure 12c. As^{+3} $5(H_2O)$ in water

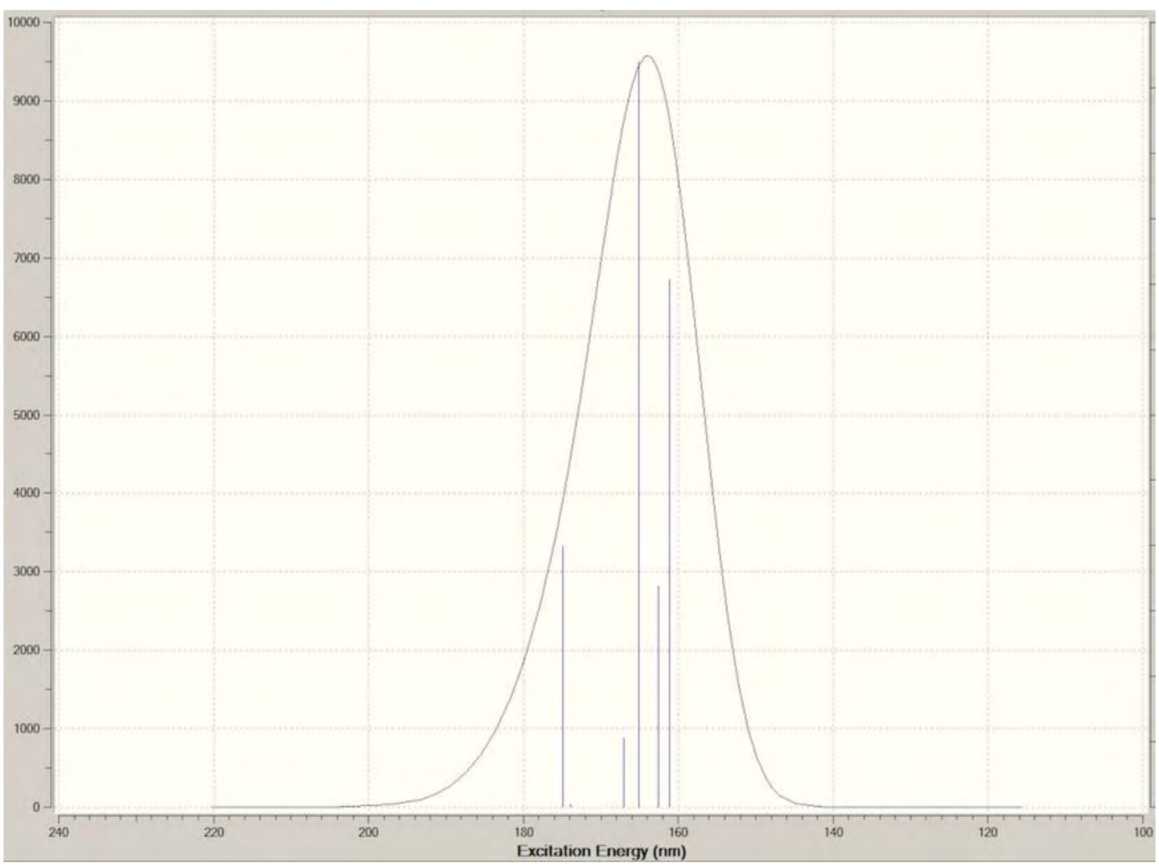

Figure 12d. As^{+3} $7(H_2O)$ in water

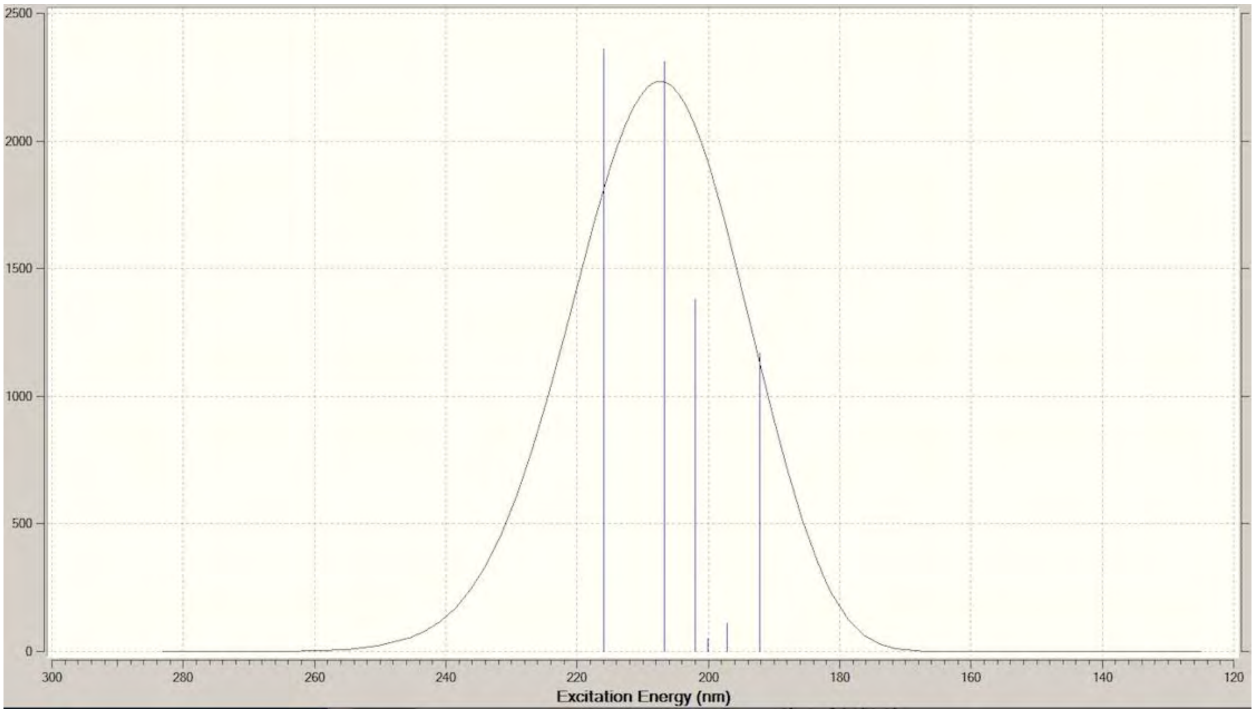

Figure 12e. As^{+3} 15(H_2O) in water

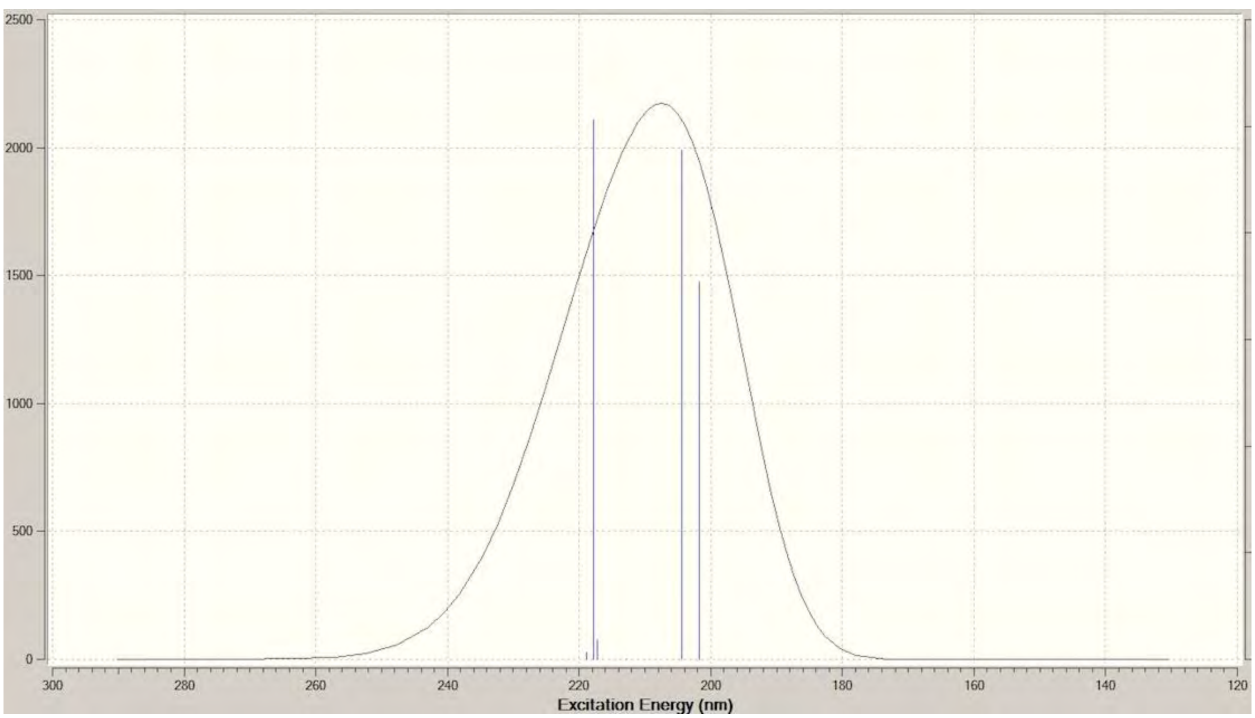

Figure 12f. As^{+3} 20(H_2O) in water

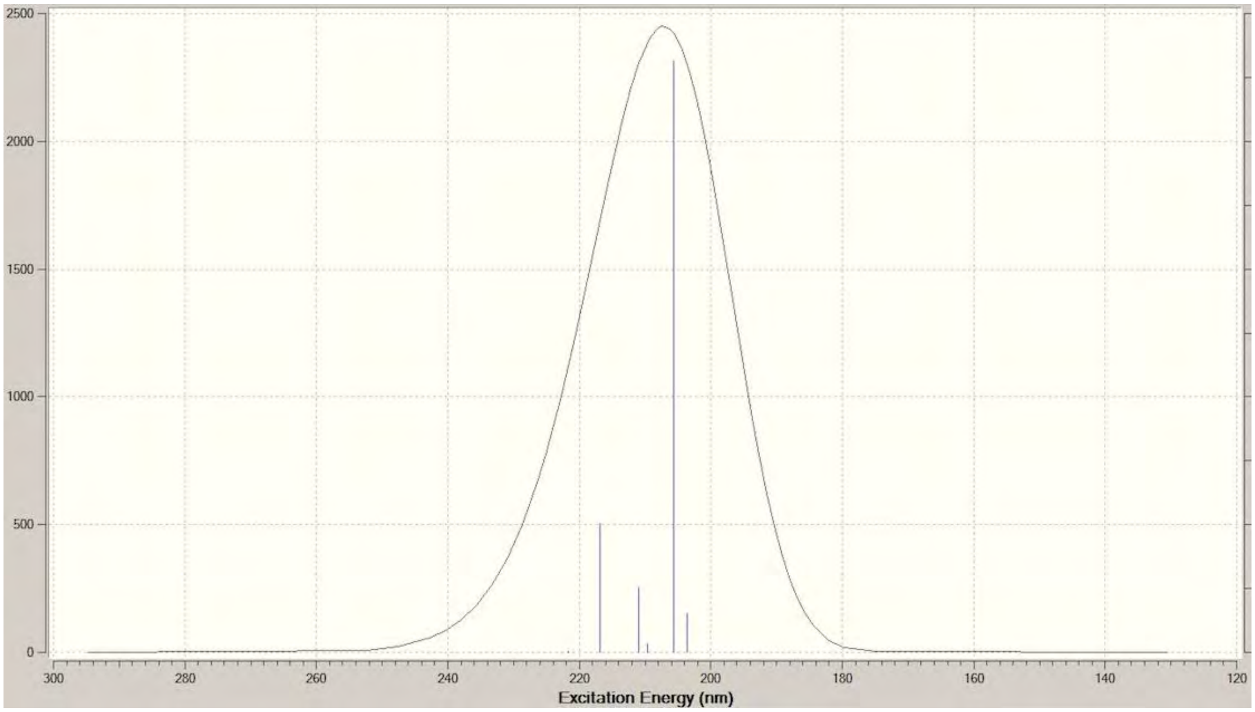

Figure 12g. As^{+3} 24(H_2O) in water

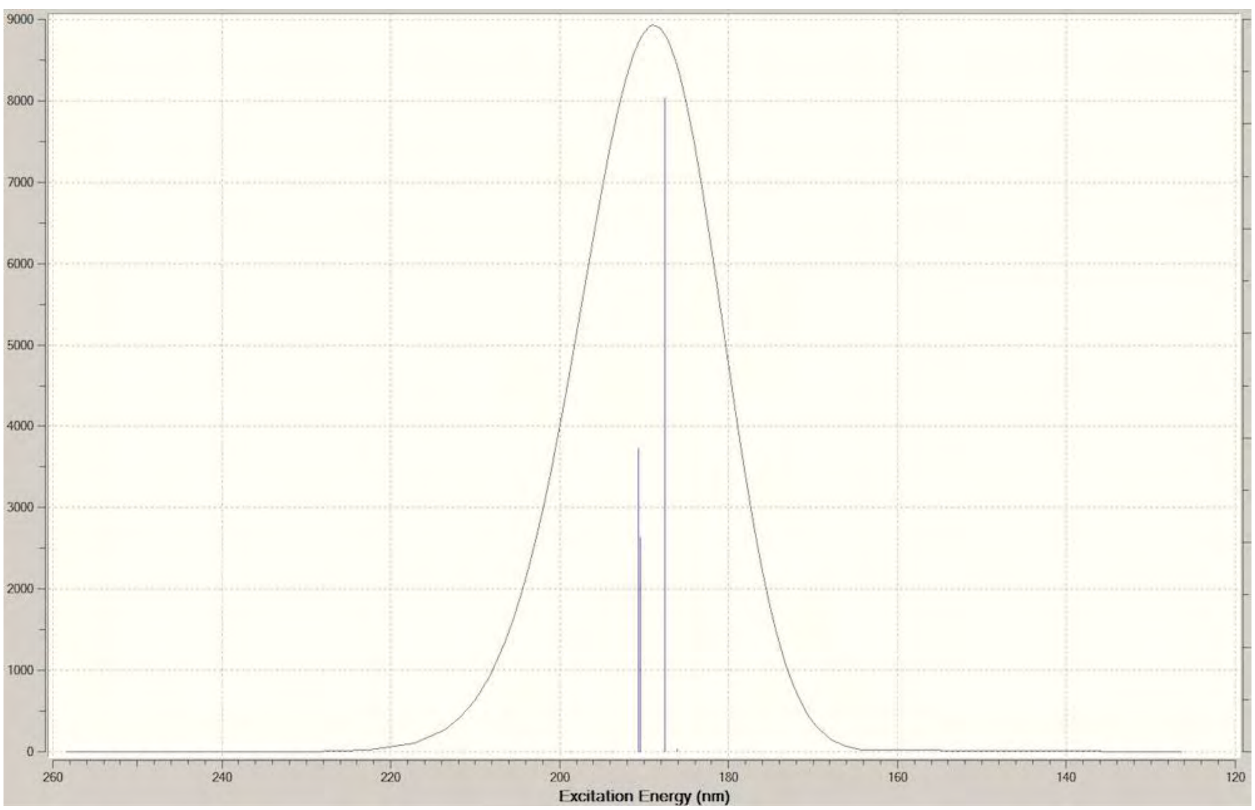

Figure 12h. As^{+3} 36(H_2O) in water

Figure 12. TD-DFT calculated UV-Visible spectra for As-H_2O complexes consisting of 2, 4, 5, 7, 15, 20, 24 and 36 water molecules, with water background. Intensity is in arbitrary units.

Table 3. Energies for optimized geometries of As^{+3} - nH_2O clusters.

Complex	Energy of As-nH_2O	Energy of As-nH_2O in water
As^{+3} $2H_2O$	-2387.1959 a.u.	-2388.0138 a.u.
As^{+3} $3H_2O$	-2463.8065 a.u.	
As^{+3} $4H_2O$	-2540.3547 a.u.	-2541.0639 a.u.
As^{+3} $5H_2O$	-2616.8885 a.u.	-2617.5571 a.u.
As^{+3} $6H_2O$	-2693.3986 a.u.	
As^{+3} $7H_2O$	-2769.9843 a.u.	-2770.5404 a.u.
As^{+3} $15H_2O$	-3381.8344 a.u.	-3382.3064 a.u.
As^{+3} $20H_2O$	-3764.2247 a.u.	-3764.6522 a.u.
As^{+3} $24H_2O$	-4070.1132 a.u.	-4070.5269 a.u.
As^{+3} $36H_2O$	-4987.7749 a.u.	-4988.1695 a.u.

Table 4a. Excited states of As^{+3} - nH_2O clusters.

Componds	**Multiplicity-Orbital symmetry**	**Excitation E**	**Oscillator strength**
As^{+3} $2H_2O$	Singlet-A	219.29nm	0.0586
	Singlet-A	192.98nm	0.0226
	Singlet-A	184.99nm	0.0519
	Singlet-A	167.68nm	0.0041
	Singlet-A	164.52nm	0.0000
	Singlet-A	152.92nm	0.0000
As^{+3} $3H_2O$	Singlet-A	184.97nm	0.0404
	Singlet-A	184.84nm	0.0413
	Singlet-A	171.53nm	0.0226
	Singlet-A	170.40nm	0.0029
	Singlet-A	167.75nm	0.0090
	Singlet-A	167.55nm	0.0095
As^{+3} $4H_2O$	Singlet-A	188.72nm	0.0008
	Singlet-A	188.49nm	0.0000
	Singlet-A	183.07nm	0.0100
	Singlet-A	181.73nm	0.0122
	Singlet-A	176.23nm	0.0352
	Singlet-A	175.27nm	0.0019

As^{+3} $5H_2O$	Singlet-A	205.08nm	0.0289
	Singlet-A	192.92nm	0.0021
	Singlet-A	189.47nm	0.0000
	Singlet-A	187.46nm	0.0566
	Singlet-A	185.75nm	0.0574
	Singlet-A	180.41nm	0.0000
As^{+3} $6H_2O$	Singlet-AU	190.25nm	0.0561
	Singlet-AU	190.17nm	0.0605
	Singlet-AU	190.10nm	0.0526
	Singlet-AG	188.43nm	0.0000
	Singlet-AG	188.31nm	0.0000
	Singlet-AG	188.02nm	0.0000
As^{+3} $7H_2O$	Singlet-A	174.88nm	0.0399
	Singlet-A	173.88nm	0.0004
	Singlet-A	167.07nm	0.0106
	Singlet-A	165.08nm	0.1140
	Singlet-A	162.56nm	0.0338
	Singlet-A	161.10nm	0.0806
As^{+3} $15H_2O$	Singlet-A	216.01nm	0.0236
	Singlet-A	206.64nm	0.0231
	Singlet-A	202.01nm	0.0138
	Singlet-A	200.15nm	0.0005
	Singlet-A	197.22nm	0.0011
	Singlet-A	192.15nm	0.0117
As^{+3} $20H_2O$	Singlet-A	218.79nm	0.0003
	Singlet-A	217.76nm	0.0253
	Singlet-A	217.26nm	0.0009
	Singlet-A	212.81nm	0.0000
	Singlet-A	204.41nm	0.0239
	Singlet-A	201.78nm	0.0177
As^{+3} $24H_2O$	Singlet-A	221.78nm	0.0001
	Singlet-A	216.87nm	0.0101
	Singlet-A	210.95nm	0.0051
	Singlet-A	209.62nm	0.0007
	Singlet-A	205.71nm	0.0463
	Singlet-A	203.55nm	0.0030
As^{+3} $36H_2O$	Singlet-A	198.73nm	0.0000
	Singlet-A	193.69nm	0.0000
	Singlet-A	190.67nm	0.0579
	Singlet-A	190.49nm	0.0410
	Singlet-A	187.53nm	0.1250
	Singlet-A	186.05nm	0.0005

Table 4b. Excited states of As^{+3} - nH_2O clusters in water background.

Componds in water	Multiplicity-Orbital symmetry	Excitation E	Oscillator strength
As^{+3} $2H_2O$ in water	Singlet-A	201.12nm	0.0561
	Singlet-A	180.51nm	0.0629
	Singlet-A	176.27nm	0.0247
	Singlet-A	153.21nm	0.0065
	Singlet-A	145.76nm	0.0009
	Singlet-A	139.70nm	0.0000
As^{+3} $4H_2O$ in water	Singlet-A	171.22nm	0.0237
	Singlet-A	168.81nm	0.0071
	Singlet-A	165.80nm	0.0196
	Singlet-A	165.10nm	0.0188
	Singlet-A	162.45nm	0.0818
	Singlet-A	160.93nm	0.0289
As^{+3} $5H_2O$ in water	Singlet-A	188.71nm	0.0546
	Singlet-A	176.82nm	0.1869
	Singlet-A	173.55nm	0.2518
	Singlet-A	167.30nm	0.0031
	Singlet-A	164.96nm	0.0011
	Singlet-A	161.51nm	0.0000
As^{+3} $7H_2O$ in water	Singlet-A	171.06nm	0.0023
	Singlet-A	170.31nm	0.0468
	Singlet-A	165.68nm	0.00172
	Singlet-A	162.22nm	0.1718
	Singlet-A	155.63nm	0.0107
	Singlet-A	154.58nm	0.0945
As^{+3} $15H_2O$ in water	Singlet-A	208.98nm	0.0765
	Singlet-A	192.00nm	0.0148
	Singlet-A	185.55nm	0.1547
	Singlet-A	184.83nm	0.0008
	Singlet-A	181.58nm	0.0007
	Singlet-A	180.88nm	0.0106
As^{+3} $20H_2O$ in water	Singlet-A	211.31nm	0.0662
	Singlet-A	188.94nm	0.0285
	Singlet-A	188.00nm	0.1147
	Singlet-A	186.81nm	0.0238
	Singlet-A	181.24nm	0.0043
	Singlet-A	180.75nm	0.0037
As^{+3} $24H_2O$ in water	Singlet-A	210.29nm	0.0687
	Singlet-A	198.28nm	0.0046
	Singlet-A	192.88nm	0.0071
	Singlet-A	190.91nm	0.0087
	Singlet-A	190.15nm	0.0031
	Singlet-A	189.15nm	0.0133
As^{+3} $36H_2O$ in water	Singlet-A	189.03nm	0.1638
	Singlet-A	187.67nm	0.1897
	Singlet-A	176.76nm	0.0021